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Development of a Low Cost Cook-Off Test for Assessing the Hazard of Explosives

ROYAL MILITARY COLLEGE OF SCIENCE

PhD THESIS

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Development of a Low Cost Cook-Off Test for Assessing the Hazard of Explosives

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This Thesis is dedicated to the memory of

Benjamin B. (Bo) Stokes III

A true example that Ethics, Passion and a Great Sense of Humour are all Science should be about.

May many others follow in Bo's path …

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Abstract

A low cost Cook-Off experimental facility has been established to provide a convenient method of ranking explosives in their response to Cook-Off by the time to event under two widely different heating rates and at two different scales. This thesis describes the literature review undertaken as preparation for the purposed study and all the experimental work developed comprising the design of the trials vehicles, the demonstration of their suitability for Fast and Slow Cook-Off trials with confined explosive systems, the preparation of the samples and test vehicles to be trialled as well as the set-up of adequate facilities to undertake the scheduled firing programme. Results are reported for Cook-Off tests on TNT, RDX, and their mixtures.

The emphasis of the study is on time to event, and temperature at event, and in addition a qualitative assessment of the violence of the event was made by examination of the fragments of the vehicles, although it is accepted that the relatively light and low cost design of the vehicle may lead to variable confinement in the early stages of the explosive event, and hence to a wider spread of responses than would be obtained from a more heavily confined and more costly vehicle.

The test vehicles give results, which differentiate between the various explosives and explosive mixtures trialled and between the scales. More experiments are required to establish the reproducibility of the measurements. The design of the equipment makes this a relatively inexpensive undertaking.

The experiment was modelled using published kinetic data, but the calculated time to event differed from that observed to different extents at the two scales. It is hypothesised that the mechanism may change over the prolonged heat soaks and that quantitative scaling is not possible with the available information.

Further work is also suggested using a different type of Cook-Off test vehicle, which will in our opinion reduce even further the cost of Cook-Off testing, due to reduction in man-hours of preparation involved and manufacture cost of the Cook-Off test vehicles, and consequently of ranking of explosives.

Chapter I

INTRODUCTION

The sensitiveness of energetic materials used in ordnance systems has always been one of the utmost important issues as it relates to the safety of handling, manufacture, storage and transportation of such systems during their entire life cycle. Furthermore, it is of continuous relevance, due to the potential damage caused by the accidental ignition of any device containing energetic materials and the impossible task of precluding its inadvertent initiation under all conceivable scenarios. The sensitivity to heat is one of the main characteristics of all energetic materials as they decompose exothermically and at a sufficiently high temperature are capable of self-heating to a very rapid, potentially violent, release of chemical energy.

The consequences of inadvertent ignition of munitions can be catastrophic – including loss of life and extensive damage to equipment (see Appendix I). Cook-Off is the most common cause of accidents with energetic materials and ordnance items and is normally the one presenting the utmost dramatic consequences. This very important subject is independent of the civil or military nature of the application of the energetic materials or even, in the case of ordnance systems, from a peace or war scenario as proven in the past by the several accidents which have occurred in civil and military facilities.

The occurrence of major accidents, particularly the fire aboard the USS Forrestal, in 1967, prompted from the beginning of the 1970s serious and extensive research projects in the U.S.A. specifically to study the cause and effects of thermal threats in relation to energetic materials and ordnance items. Other countries like the U.K. embraced similar programs at around the same time. Gradually the development of mitigation devices and materials to increasingly reduce the violence of response from an item under thermal threat became a major part of these research programs.

The main types of stimuli that have caused accidents are either heat or impact. In war scenarios, the threats to ordnance systems are even greater as enemy fire threatens them with thermal and impact stimuli from bullets and the fragment products of detonation devices. Therefore, the loss of platforms and other types of equipment in battle is often due to the secondary reactions of their own munitions following initiation by enemy fire (Boggs & Derr, 1990).

Cook-Off is defined as "the response of energetic materials in weapon systems that are exposed to abnormal thermal environments" (Stokes III, 1993). Originally the designation of *Cook-Off* was applied to the specific situation of a cartridge within a gun being ignited by the heating of the hot breech. With the development of energetic materials with increasing energy content, the meaning of Cook-Off has broadened and now is concerned with how energetic materials and ordnance systems react to thermal stimuli ranging from exhaust impingement or Fuel Fires (Fast Cook-Off) to bulk heating or self-heating (Slow Cook-Off). One can consider two different types of the Cook-Off phenomena, depending on the gradients dT/dx and heating rate dT/dt (besides the thermal source): Slow Cook-Off and Fast Cook-Off (Boggs & Derr, 1990).

The main threat to munitions is fire, as it is the most common of the thermal threats and the one with very severe consequences (Fleming, 1995; NIMIC, 1993).

The principle thermal heating sources are (Boulay, 1997): Chemical Reactions, Fuel Fires (Inflammable Liquids, Wood, Aluminium, and Steam), Adjacent Stores (Energetic Materials) and Non-Chemical Sources (Nuclear, Solar Radiation, Hot Gun, Aerodynamic, and Exhaust Gases).

There are several factors that affect the violence of response of an energetic material or an ordnance system when submitted to a thermal stimuli: energetic material composition (the chemistry of the explosive, inert additives, catalysing materials, coating materials), thermal gradients, confinement, system dimensions (size and surface area/volume), location of the external stimuli (within the energetic material or system), energetic material damage, non-energetic material effects (e.g. liner degradation) and obviously the environment (NIMIC, 1993; Dagley *et al.*, 1989a and 1989b; Dagley *et al.*, 1996). The influence of one of these factors might be strong enough to control the violence of response of the system to the thermal stimuli.

In order to assess this type of response to unplanned thermal stimuli, several different types of experimental devices were designed and constructed throughout this research field for both Slow and Fast Cook-Off phenomena. The experimental tests are too far removed from events that occur in the real world scenarios both because the instrumentation is intrusive and may affect the results, and also because of the uncertainties of quantitative estimation of the scaling. On the other side, large scale testing has enormous costs, so that few tests can be performed and statistical significance is low. Furthermore, they provide very limited data that are, simultaneously, specific to a limited range of thermal environments and highly weather dependent. In either case, care must be taken when interpreting the results obtained with such experimental apparatus and generalising them to other systems, as most of the results are totally dependent of the system tested and the experimental conditions on which the tests were conducted.

Modelling has been considered as a possible solution for the reliable prediction of the severity of response of energetic materials and ammunition systems to unplanned stimuli. It is a very cost effective tool as it allows the assessment of a wide range of thermal environments and thermal histories of the systems, at relatively low cost. Development and validation of the models constitute the main problems of this field.

The nature of the thermal response of energetic materials or ammunition systems depends on the extent of the transition from burning through deflagration (and the formation of the compressive shock waves) to detonation at the time that overpressure caused by the gaseous products relieves the confinement. Moderation of the Cook-Off response requires controlled or inhibited burning reactions at increasing pressures, improved resistance to fracture under shock compression to reduce explosiveness, reduction of the shock sensitivity of the explosive or combinations of these (and other) approaches designed to avoid the occurrence of deflagration-to-detonation transition. Due to the complex nature of these processes and the experimental difficulties in studying these events, the understanding of the mechanisms involved in Cook-Off reactions and how to achieve moderate responses is reduced (Dagley *et al.*, 1996).

1.1. INITIATION OF ENERGETIC MATERIALS

The initiation of energetic materials other than by high energy shock (e.g. from a detonating donor explosive) is normally considered to be thermal in origin (Bowden & Yoffe, 1956; Field *et al.*, 1982, 1992; Field, 1992), irrespective of the type of stimulus applied: mechanical (impact, shock, and friction), thermal (fire, climate conditions) or electrical (spark).

Field *et al.* (1982, 1992) consider that the energy involved in mechanical or electrical processes is normally converted into heat in localised sites, thus inducing the formation of “hot spots”. This can happen via a variety of mechanisms and several mechanisms for the formation of “hot spots” have been proposed over the years. These authors also agree that there is not a single dominant mechanism controlling this process as the way in which the mechanisms develop depends strongly on the energy input and on the physical properties of the explosive system. Furthermore, it is stated that when considering any specific explosive system it is important to comprehend the various “hot spots” formation mechanisms and the properties of the explosive, i.e., mechanical, thermal and chemical.

Field (1992) states that when considering critical “hot spots”, their sizes, temperatures and durations are interdependent. Bowden & Yoffe (1956) present values for the size, duration and temperature of the “hot spot” of the order 10^{-4} - 10^{-1} mm in diameter, of 10^{-5} - 10^{-3} s and of about 773 K. The “hot spot” temperature is appreciably higher than the conventional ignition temperature, which for many explosives heated in bulk is about 473 - 523 K.

The main mechanisms that have been suggested for ignition, involving the conversion of mechanical or electrical energy to thermal energy, are (Field *et al.*, 1982 & 1992; Field, 1992):

- adiabatic compression of trapped gas spaces;
- mechanisms involving cavity collapse, such as viscous or plastic heating of the surroundings of the matrix material or, for very high shock collapse pressures, hydrodynamic shock focusing;

- friction between sliding or impacting surfaces, or between explosive crystals and/or grit particles in an explosive;
- localised adiabatic shear of the material during mechanical failure;
- viscous heating of material rapidly extruded between impacted surfaces;
- heating at crack tips;
- heating at dislocation pileups;
- spark discharge;
- triboluminescent discharge;
- decomposition, followed by Joule heating of metallic filaments.

Other mechanisms based on tribochemical or molecular fracture have been suggested with little experimental support.

In the present study is concerned specifically with heat flux as the thermal process which may lead to the ignition of the explosive systems.

1.2. TYPES OF COOK-OFF EVENTS

The main Cook-Off stimulus is fire, as it is the most common of the thermal threats and, simultaneously, the one with more severe consequences whatever concerns the response of energetic materials and ordnance systems when accidentally submitted to it (Fleming, 1995; NIMIC, 1993).

In the case of ammunition systems, the presence of readily ignited fuels and a wide variety of ignition sources during deployment and transportation (and when in a war scenario the threat of enemy action) provides the potential for fires, which may engulf munitions. In other cases the cause for Cook-Off events is due to the munitions' cyclic thermal loading while being transported or stored (Fleming, 1995; Farinaccio, 1991).

One of the main concerns is the situation where a munition is heated slowly by a fire in an adjacent compartment. Such incidents can escalate rapidly particularly in confined spaces, as is the case in magazines and embarked naval stores (Fleming, 1995). The violence of response in such a case is normally very high as proved by several accidents in the past.

It should be noted that in simulating realistic situations or stimuli, the munitions might be exposed to a Cook-Off mechanism, which can be a combination of Slow and Fast Cook-Off, or even an intermediate other than these. An example of this would be the heat transfer from a hot gun barrel to a lodged munition casing (Farinaccio, 1991).

The complexity of the Cook-Off mechanism is also dependent on the degree of confinement and the mass of the explosive (Farinaccio, 1991).

1.2.1. Slow Cook-Off

By *Slow Cook-Off* is understood "the reaction mechanism which occur in a munition as a result of a slow heating stimulus" (NIMIC, 1998; AOP IM).

For slow heating rates all the energetic material is at an elevated temperature with a minimal thermal gradient throughout its mass until self-heating occurs which raises the temperature preferentially near the centre of the charge (NIMIC, 1993). This is due to the thermal conductivity of the explosive which is lower than that of the case.

Dagley *et al.* (1996) refer that a very slow heating rate, corresponding to prolonged indirect exposure to a heat source, leads to thermal equilibration across the explosive and in this case a more central ignition occurs.

The main factors affecting the response to such a stimulus are the degree of confinement of the energetic material, its explosiveness[1], the extent of physical and chemical degradation of the energetic material, the diameter/dimension of the ordnance system and the location of the ignition point under such confined conditions (NIMIC, 1993). Another factor of major importance in the Slow Cook-Off phenomenon is the thermal conductivity of the filling as this parameter contributes to the violence of the response mechanism.

The temperature during the reaction of the explosive at low ambient conditions is usually less than that experienced at high heat environments. The thermal decomposition of the explosive proceeds slowly at low ambient conditions and the heat transfer is efficient since most of the heat generated in the environment is transferred to the explosive (Farinaccio, 1991).

[1] *Explosiveness* is "a measure of the explosive response to a given stimulus in a defined system. It describes a degree of violence shown by an explosive material when it responds to a prescribed stimulus relevant to an accident situation" (Sensitiveness Collaboration Committee, 1988).

In spite of the fact that the original concept of Slow Cook-Off (SCO) was based on the idea of an undetected fire in an adjacent compartment on a ship or land based storage magazine, this has been proved unrealistic not only from the point of view of the heating rates involved, but also from the improbability of such an event. Nevertheless, because it was observed, in the majority of the cases, that Slow Cook-Off produces a more severe response (as it is a bulk phenomenon initiated deep inside the charge and the charge mass acts as confinement itself) than Fast Cook-Off (FCO) (as these result from a phenomenon taking place on the surface of the charge), it was considered useful to obtain as much significant information as possible to both extremes of the heating rate. To a certain extent, Slow Cook-Off tests can be considered a form of large-scale stability and compatibility tests on the energetic material in ordnance systems (NIMIC, 1993).

Fleming refers experimental work done with the ODTX apparatus at intermediate applied temperatures, in which a large deformation of the cavity is observed and the aluminium surface becomes patinated, indicative of high temperatures. Calculations indicated that thermal runaway occurs near the centre of the explosive sample after it has reached a nearly uniform temperature. Once ignition occurs the high local inertial confinement and the relatively high temperature of the bulk explosive allows rapid and almost complete combustion before confinement failure. This thermal environment, which is equivalent to Slow Cook-Off in a munition, results in a violent and highly disruptive explosive event (Fleming, 1995).

He also referred that for low applied temperatures the ODTX anvils show relatively little damage and that calculations indicate that no thermal runaway occurs at these temperatures, and that the explosion results from the build up of thermal decomposition products. In munitions, this situation would be translated as a degree of damage dependent on the strength of the case and the effects would be expected to be localised (Fleming, 1995).

1.2.2. Fast Cook-Off

Fast Cook-Off is defined as "the reaction mechanism which occurs in a munition as a result of a fast heating stimulus" (NIMIC, 1998; AOP IM).

This type of reaction typically occurs in ordnance systems because the heat source ignites the energetic material close to its external surface (NIMIC 1993).

Dagley *et al.* (1996) refer that a fast heating rate, which corresponds to direct exposure to a Fuel Fire, results in a large radial temperature gradient across the explosive and ignition at or close to the surface of the explosive.

The main factors affecting the response to such a stimulus are the degree of confinement of the energetic material and its explosiveness (NIMIC, 1993).

For high heating rate environments such as Fast Cook-Off, the generated heat is dissipated and the heat transfer is less efficient than a situation of Slow Cook-Off (Farinaccio, 1991), thus creating high temperature distribution gradients throughout the mass of the explosive system.

Fleming refers that at high applied temperatures in ODTX experiments the anvils show relatively little damage and in some cases the majority of the explosive remain in the separated anvils. In these cases the calculations indicate that thermal runaway occurs at the surface of the charges at a time when the bulk explosive is relatively cool. This suggests that rapid decomposition at the hot outside surface produce sufficient gas to disrupt the confinement, which quenches the reaction before propagation to the bulk explosive occurs. This thermal environment, which is equivalent to rapid heating of a munition system, results in a relatively mild explosive event (Fleming, 1995).

1.3. STUDY PROGRAM

The Department of Environmental and Ordnance Systems (D.E.O.S.) at the Royal Military College of Science, Cranfield University, has much experience in the area of explosives safety-related research. The response of explosives to the different kinds of stimuli encountered in accidents, which occur during the handling, storage and transport of explosives and explosives ordnance is not well understood in detail and yet the development of adequate safety regulations and appropriate legislation depends on such understanding.

Current tests concentrate on measuring the violence of response due to accidental initiation leading to Cook-Off. Furthermore, because of the high cost of ordnance and the associated testing, very few trials are carried out. Data from such trials are not therefore statistically significant.

The establishment of a permanent test facility for Cook-Off testing at the Royal Military College of Science and the development of a low cost Cook-Off test for assessing the hazard of explosives were the two main aims of this research project.

The Cook-Off test vehicle was designed and constructed to very specific requirements of an Explosives Safety Related Project. These requirements were the use of low cost and readily available materials, the scaling up of the test vehicles and the flexibility of change of any features of the test vehicle (e.g. bolts, wall thickness) in order to allow for a variety of thermal studies.

This PhD programme aimed to develop a low cost scalable Cook-Off test facility that will allow for rapid ranking of explosives with respect to their time and temperature to Cook-Off, and for a wide range of Cook-Off studies concerning the various parameters that play a major role in the Cook-Off phenomenon: confinement, composition and mass of energetic material system under study, dimensions of the charge, etc..

The present research programme had the following main aims:

(i) research, design and construct an experimental Cook-Off facility for studying the response (time to reaction, temperature at event and violence of reaction) of explosives to heat, using samples in the 0.02 - 0.20 kg range;

(ii) research, design and construct a Cook-Off test vehicle that will allow scale up studies;

(iii) perform the necessary tests in order to assess of the capability of the Cook-Off facility and the Cook-Off test vehicle to comply with the experimental procedures comprised by the NATO Standard Agreement for this type of ordnance items testing;

(iv) select and thoroughly characterise the explosive systems to be tested for Cook-Off purposes;

(v) analyse the collected data to obtain kinetic decomposition parameters, which will then be used to test computer models in order to allow the prediction of the explosive response.

The abovementioned programme of work necessitated the development of a good understanding of sensors for the measurement of transient events and the related instrumentation, and the application of this knowledge.

The explosive systems selected to perform Cook-Off studies on the effect of scale and heating rate in order to assess the suitability of the Cook-Off test being set up to allow for Cook-Off studies with a wide variety of parameters were: RDX, TNT and RDX/TNT mixtures.

A brief summary of the thermochemical characteristics of the single explosives is presented below.

1.3.1. RDX

cyclo-1,3,5-trimethylene-1,3,5-trinitramine (synonyms: hexahydro-1,3,5-trinitro-*s*-triazine, *cyclo*trimethylenetrinitramine, 1,3,5-trinitro-1,3,5-triazacyclohexane, trimethylene-trinitramine, Cyclotol, Cyclonite) was first synthesised by Henning in 1899, recognised as an explosive by Herz in 1920, and developed as a practical explosive only before World War II (WWII) by scientists in the Research Department at Woolwich Arsenal, London, U.K. (Research Department eXplosive).

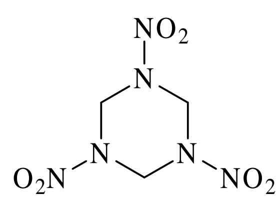

Figure 1.1 - The Chemical Structure of RDX.

It is prepared by the nitration of hexamethylene tetramine. The first industrial process to be developed (the Woolwich Process) produces a very pure product, but is less economical than the Bachmann Process which produces higher yields of a material contaminated with variable amounts of the more powerfully explosive homologue *cyclo*-1,3,5,7-tetramethylene-1,3,5,7-tetranitramine (HMX).

Whatever the synthetic route, the material is purified by recrystallisation from an organic solvent such as *cyclo*hexanone. It is a white, odourless solid reasonably stable at temperatures up to its melting point.

For military use RDX is usually desensitised with wax, TNT or a polymeric binder before being filled into munitions. RDX/TNT (usually 60/40 with an additional 1% wax) has been the standard main charge for fragmenting munitions since WWII. RDX/wax 88/12 is a very insensitive explosive for High Explosive Squash Head (HESH) projectiles which must survive crushing after impact without initiation; RDX/wax 95/5 is a much more sensitive material used for boosters; RDX/wax 99/1 is a sensitive material used in narrow stemmings as part of the initiation train.

Some properties of RDX are given in Table 1.I:

Empirical Formula	$C_3H_6N_6O_6$
Molecular Mass	222.1
ΔH_f	+318 kJ kg^{-1}
	+70.6 kJ mol^{-1}
Oxygen Balance	-21.6%
Melting Point	477.2 K
Heat of Explosion (H_2O Liquid)	5757 kJ kg^{-1}
	1260 kJ mol^{-1}

Table 1.I - Properties of RDX.

RDX has a negative oxygen balance, and the equation for the formation of detonation products can be written following the procedure of Kistiakowsky and Wilson:

$C_3H_6N_6O_6 = 3CO + 3H_2O + 3N_2$

Taking ΔH_f (CO) = -110.5 kJ mol^{-1}, and ΔH_f ($H_2O(l)$) = -285.8 kJ mol^{-1}, the value for the heat of formation of RDX quoted above then leads to a heat of explosion of 1260 kJ mol^{-1}.

1.3.2. TNT

2,4,6-trinitrotoluene (synonyms α-TNT, trinitrotoluene, trinitrotoluol, trotyl, tolite) is one of the oldest of "modern" explosives because of its fairly good explosive output, its relative safety in use, and its conveniently low melting point which allows it to be cast into munitions and used without desensitisers; indeed it is itself used as a desensitiser for RDX as mentioned above. Pressed crystalline TNT is more shock sensitive than cast, and is used commercially in large quantities as boosters and sensitisers for highly insensitive slurry explosives.

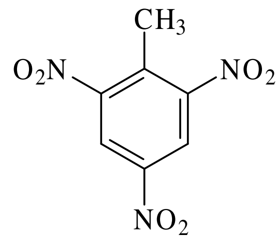

Figure 1.2 - The Chemical Structure of TNT.

The properties of TNT are given in Table 1.II. Particular attention is drawn to the setting point. Because of the large volume of TNT in many munitions, even a small amount of impurity (particularly di- and mono-nitrotoluenes) can produce low melting eutectics which can migrate on hot storage. Good quality military TNT is therefore very pure, and has a high set point.

Empirical Formula	$C_7H_5N_3O_6$
Molecular Mass	227.1
ΔH_f	-261.5 kJ kg^{-1}
	- 65 kJ mol^{-1}
Oxygen Balance	-73.9 %
Melting Point	354 K
Heat of Fusion	+96.6 kJ kg^{-1}
	+21.9 kJ mol^{-1}
Heat of Explosion (H_2O Liquid)	4564 kJ kg^{-1}
	1036 kJ mol^{-1}

Table 1.II - Properties of TNT.

TNT is has a strongly negative oxygen balance, and the following equation obeys the Kistiakowsky-Wilson rules:

$C_7H_5N_3O_6 = 3.5CO + 2.5H_2O + 3.5C + 1.5N_2$

The enthalpy of formation may therefore be calculated as - 65 kJ mol^{-1} on the basis of an experimental heat of explosion (water as liquid) of 4564 kJ kg^{-1} (1036 kJ mol^{-1}) (Köhler & Meyer, 1993).

Chapter II

LITERATURE REVIEW

In this Chapter a literature search is presented which addresses the main aspects involved in the Cook-Off of energetic materials and ordnance items: Cook-Off theory, factors affecting Cook-Off, experimental assessment of Cook-Off and modelling.

2.1. THEORY OF COOK-OFF

N.N. Semenov (1928) was the first to establish the Thermal Explosion Theory, treating the special case of a system with uniform temperature. Frank Kamenetskii (1939) developed the theory in order to encompass systems with distributed temperatures and allow for the treatment of regular shapes of reactants, e.g., infinite slab, the infinite cylinder and the sphere.

Over the years, many other authors have addressed the Thermal Explosion Theory. Especial reference is made here to the reviews by Merzhanov & Dubovitskii (1966), Gray & Lee (1967), Gray & Sherrington (1977), Merzhanov & Abramov (1981), Boggs & Derr (1990) and Lee (1998) and their contributions to this topic.

Feng published extensively on thermal explosions theories, namely a new approach to the theories in 1985, a book (in Chinese) in 1988, with all the developments of the theory until 1986 and later some more developments on the theories and behaviour of uniform temperature systems at the point of criticality (1991a, 1991b). In 1994, Feng *et al.* made a significant contribution by applying a numerical model to the investigation of two-dimensional thermal explosion criteria and the centre dimensionless temperature under the critical state to exothermic reaction systems with infinite tetrahedral rod and finite cylinder geometrical shapes (1994a and 1994b).

An especial mention has also to be made to the contributions for the study of thermal explosion theory by Boddington *et al.* (1977, 1982, 1983, 1984, 1986), Scott (1984) and Creighton (1994). Boddington *et al.* presented studies on criteria for thermal explosions with and without reactants consumption. These authors also present a new criterion for criticality of thermal explosions with extensive reactant consumption. Further modelling includes thermal runaway and criticality in systems with diminishing reaction rates, thermal explosions with simultaneous parallel reactions, and finally the study on the influence of a steadily increasing (ramped) ambient temperature on thermal explosion and times to ignition in systems with distributed temperatures.

Scott (1984) developed modelling into thermal explosions of dispersed media, i.e., discrete reactive particles in a reactive matrix.

Similarly to Boddington *et al.* (1986), Creighton (1994) analysed a linear temporal increase of the surface temperature, but in a more realistic fashion involving multi-step reaction schemes representing some real explosives (HMX and TATB). The results obtained, which are similar to the constant boundary temperature with the exception that at higher heating rates the ignition temperature is higher than the critical temperature, present numerical solutions to the multi-step reaction schemes.

There will be no detailed analysis of these studies presented here, due to the complexity of the mathematical models developed. However, the basic Thermal Explosion Theory according to Semenov and Frank Kamenetskii, and its significance for the Cook-Off studies will be discussed.

Energetic materials such as explosives and propellants undergo exothermic thermal decomposition. Two different types of situation might occur (Merzhanov & Abramov, 1981; Lawton & Kligenberg, 1996):

- if the surroundings of the system are maintained at a low temperature, and there are favourable conditions for heat transfer processes, the reaction in the system will proceed at a slow rate, the heat generated will be removed from the system, thus establishing a temperature equilibrium between the system and the surroundings;

- if, on the other hand, the heat transfer conditions are such that the heat released by the chemical decomposition is stored in the system rather than dissipated to the surroundings, the increasing temperature accelerates the rate of the reaction until the process becomes explosive.

The temperature at which thermal explosion occurs depends on the properties of the reactant, quantity of the reactant and the heat transfer conditions between the system and the surroundings (Merzhanov & Abramov, 1981; Frota, 1995; Lawton & Kligenberg, 1996).

The thermal decomposition of explosives and propellants is assumed to follow an Arrhenius Equation, where the rate of decomposition (k) depends on the activation energy, E, the rate constant, A, and the absolute temperature, T. The activation energy, E, and the rate constant, A, are characteristic for a given material and are usually assumed to be constant.

$$k = Ae^{\left[\frac{-E}{R_o T}\right]} \quad (s^{-1}) \qquad [2.1]$$

As Soviet researchers made the major contributions to the Thermal Theory, this literature review will follow their work closely as did the review presented by Boggs & Derr (1990). The simple Theory of Thermal Explosion described by these authors and by Merzhanov & Abramov (1981) considers that heat is generated within the body of a material as a result of chemical decomposition activated by high temperatures. Several assumptions are considered (Merzhanov & Abramov, 1981; Boggs & Derr, 1990):

- Radiation can be neglected;

- The reaction taking place is a zero-order reaction, i.e., its rate is independent of the concentration of the reactant;

- Uniform temperature distribution in the reactant;

- All other parameters of this process remain constant (shape and size of the sample, ambient temperature, heat transfer with the surroundings, etc.).

Considering the above conditions, the heat balance can be described as follows:

$$C\rho \frac{dT}{dt} = Q\rho k_0 e^{\frac{-E}{RT}} - \frac{\alpha S}{V}(T - T_0) \quad [2.2]$$

where C is the heat capacity of the reactant, ρ the density of the reactant, T the temperature of the reactant, T_0 the ambient temperature, t the time, Q the heat of reaction, k_0 the pre-exponential factor, E the activation energy of the reaction, α the heat transfer coefficient, S the area of the heat transfer surface and V the reactant volume.

The left hand-side term of Equation [2.2] denotes the heat accumulation rate in the reactant while, on the right hand-side term, the rate of heat generation due to the reaction and of heat loss to the surroundings are expressed. The most significant attribute of this Equation is the exponential dependence of the heat generation on the temperature, which determines the characteristic properties of the phenomenon.

The mathematical analysis of the heat balance equation was first attempted by Semenov (1928), who is also responsible for laying the foundation of the Thermal Explosion Theory. In this context, a comparison of the dependences of heat generation and heat loss rates on temperature in the diagram "$\dot{q}$-T" also often designated by Semenov Diagram (Fig. 2.1). This diagram presents the regimes of the reaction that are thermally viable:

- The heat generation curve, $\dot{q}_{rel} = Q\rho k_0 e^{\frac{-E}{RT}}$, intersects the heat loss straight line, $\dot{q}_{rem} = \alpha S(T - T_0)/V$, in the region of low temperatures (curve, Fig. 2.1). The reactant is maintained at constant temperature, which corresponds to the lower point of intersection (T_1 in Fig. 2.1). This temperature is close to the ambient temperature T_0. To realize a similar regime, the difference of the initial reactant temperature from T_0 should not be significant (the initial temperature must not be higher than T_2 corresponding to the second intersection point);

- The heat generation curve does not intersect the straight line of heat loss in the low temperature region (straight line T_3). The superiority of heat generation rate over the heat loss results in progressive self-heating of the reactant to very high temperatures and thermal explosion occurs.

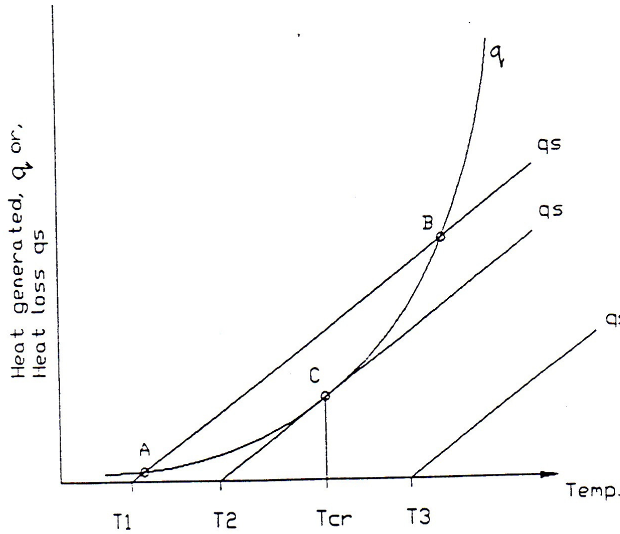

Figure 2.1 - Semenov Diagram.

The critical condition for thermal explosion is the tangency between the heat generation curve and the heat loss straight line (straight line T_2). At the tangency point T_*:

$$\dot{q}_{rel} = \dot{q}_{rem} \tag{2.3}$$

$$\left.\frac{d\dot{q}_{rel}}{dT}\right|_{T=T_*} = \left.\frac{d\dot{q}_{rem}}{dT}\right|_{T=T_*} \tag{2.4}$$

Hence,

$$\frac{Q\rho V}{\alpha S} k_0 e^{\frac{-E}{RT_*}} = (T_* - T_0) \tag{2.5}$$

$$T_* - T_0 = \frac{RT_*^2}{E} \tag{2.6}$$

The value of RT_* for explosives and propellants is usually less than the activation energy, E. Thus,

$$T_* \approx T_0 \neq \frac{RT_0^2}{E} \tag{2.7}$$

$$\frac{Q\rho V}{\alpha S}\frac{E}{RT_0^2} k_0 e^{\frac{-E}{RT_0}} \approx \frac{1}{e} \tag{2.8}$$

Equation [2.7] expresses the reactants maximum temperature in the non-explosive regime. It demonstrates that it differs from the ambient temperature by

$$\Delta T_* \approx \frac{RT_0^{\ 2}}{E} \qquad [2.9]$$

this being the maximum pre-explosive (or characteristic) temperature rise. For explosives and propellants, this temperature rise is usually about 283 - 293 K.

Equation [2.8] is a critical condition of thermal explosion. The left hand side contains all the main parameters that determine the thermal regime of the process. Merzhanov & Abramov (1981) denote it as Se in recognition of Semenov's great contribution to the development of the Theory of Thermal Explosion. Briefly it can be said that the process develops without explosion at $Se < Se_{cr}$; an explosion is prone to occur for $Se > Se_{cr}$ and $Se_{cr} \simeq 1/e$ is the critical value of Se.

Under conditions of non-uniformity of the temperature distribution of the system, one must resort to Frank-Kamenetskii's (1939) treatment of the Thermal Explosion with temperature gradients within the reactant (Merzhanov & Abramov, 1981; Boggs & Derr, 1990).

This case is better described by an equation of heat conduction with continuously distributed heat sources due to chemical reaction:

$$C\rho \frac{\delta T}{\delta t} = Q\rho k_0 e^{\frac{-E}{RT}} \phi(\eta) + div \lambda grad T \qquad [2.10]$$

where λ is the thermal conductivity.

Frank-Kamenetskii also assumes a zero-order reaction with $\varphi(\eta) = 1$. All the main parameters are placed into a complex designated by FK[2]:

$$FK = \frac{Q\rho}{4\lambda} \frac{E}{RT_0^{\ 2}} d^2 k_0 e^{\frac{-E}{RT_0}} \qquad [2.11]$$

where d is a characteristic dimension of the sample.

This characteristic dimension of a sample can be either the thickness of a slab or the diameter of a cylinder or a sphere. The surface temperature is assumed constant.

[2] Merzhanov & Abramov (1981) and Boggs & Derr (1990) designate Frank Kamenetskii's Criticality Condition by Fk. According to Merzhanov & Abramov (1981), Se is used to designate the Critical Condition of Semenov's Thermal Explosion Theory. Therefore, it seems more sensible to us to describe Frank Kamenetskii's Criticality Condition by FK, instead of Fk, designation that will be adopted throughout this literature review.

The analysis of the above equation shows that if FK < FK_{cr}, a steady temperature profile with a maximum in its centre is set up in the reactant, thermal explosion occurring when FK < FK_{cr}. Therefore, it is possible to consider that the critical condition for thermal explosion under thermal gradient conditions assumes the form

$$FK_{cr} = \frac{Q\rho}{4\lambda}\frac{E}{RT_0^{\ 2}} d_{cr}^{\ 2} k_0 e^{\frac{-E}{RT_0}} \tag{2.12}$$

The sample geometry has an influence on FK_{cr} and on the maximum pre-explosive temperature. The quantification of this influence has been established for some geometries of sample (Table 2.I):

Geometry of Sample	**FK_{cr}**	$\Delta T_* \, E / RT_0^{\ 2}$
Slab	0.88	1.2
Cylinder	2.00	1.37
Sphere	3.32	1.6

Table 2.III - Effect of Sample Geometry on Critical Conditions.

Some authors designate Frank-Kamenetskii's Criticality Criterion by δ (see Boddington *et al.*, 1977, 1984, 1986; Scott, 1984; Lee, 1998), which is not exactly the same as FK as defined above. According to Lee (1998), this is a parameter that describes the explosive type as it encapsulates the decomposition kinetics and thermochemistry as well as the shape and mass of the explosive, expressed by the following equation:

$$\delta = \left(\frac{Q}{\lambda}\right)\left(\frac{E}{RT_0^2}\right) r_0^{\ 2} A c_0 \exp\left(-\frac{E}{RT_0}\right) \tag{2.13}$$

where Q is the heat output of a decomposition reaction, λ the thermal conductivity of the reacting explosive, r_0 the characteristics linear dimension of the sample (either half-width or radius), A the frequency factor in the Arrhenius reaction rate expression, and c_0 the initial concentration of the reactant.

The same author refers that for $\delta > \delta_{max}$ there are no steady-state solutions to Equation [2.13], i.e., there is no stable temperature profile and thermal ignition occurs.

Thus, δ_{max} is identified with the critical explosion criterion δ_{crit}. This latter parameter has a unique value for each of the geometrical forms (see FK values in Table 2.I) and is associated with the largest stable temperature possible in the centre of the explosive sample.

The expression for δ_{crit} is derived from the expression firstly obtained by Groocock (1958) and quoted by Lee (1998):

$$\delta_{crit} = \frac{1}{e}\frac{\chi r_0^{\ 2}}{\lambda}\frac{S}{V} \qquad [2.14]$$

with e being the base of Naperian or natural logarithms (2.71828…), λ the thermal conductivity of the reacting explosive, χ the surface heat transfer coefficient between the reactant and the surroundings, r_0 the characteristic linear dimension of the sample (i.e. either half-width or radius), S the surface area of the reactant and V the volume of the reacting material.

Semenov and Frank Kamenetskii regarded their theories as separate and conflicting. Lee (1998) attributes to Gray & Harper (1959) the demonstration that these theories are in fact the extremes of a continuous single theory. This continuous single theory conditions can be encapsulated by the values of a parameter designated as the Biot number that can be expressed as Bi or α:

$$Bi = \frac{\chi r}{\lambda} \qquad [2.15]$$

where χ is the surface heat transfer coefficient from the Semenov theory, r the characteristic linear dimension of the sample (i.e. either half-width or radius), and λ the thermal conductivity of the explosive.

The Biot number is a measure of the internal and external heat flow resistances. Two extreme situations are possible:

- $Bi \rightarrow 0$, therefore the thermal conductivity of the reactant is very high and the surface heat transfer coefficient is small. This case reflects the Semenov's condition as all the heat flow resistance is located at the surface of the explosive;
- $Bi \rightarrow \infty$, then the thermal conductivity is small and the surface heat transfer coefficient is small. This is the case of the Frank Kamenetskii's condition.

Cook-Off testing resulted from the necessity of assessing bulk thermal hazards, and firstly involved Fuel Fire Testing[3] of ordnance items. Presently it comprises Slow and Fast Cook-Off Testing.

Considering the thermal fields, there are noticeable differences between the tests above mentioned: Fuel Fire is likely to present non-uniform and unsymmetrical thermal field while, in the case of a Slow Cook-Off, the thermal field can be considered relatively uniform. Furthermore, in the Fuel Fire case there is an initial phase of rapid heating of the sample from room temperature to the flame temperature, followed by the self-heating of the sample, due to its exothermic decomposition (Lee, 1998).

According to Lee (1998), the first attempt to solve numerically the non-steady state equations was made by Zinn & Mader (1960) followed by Merzhanov *et al.* (1963): these analyses allow the understanding of the phenomena associated with Fuel Fires and Slow Cook-Off in qualitative terms. Zinn & Mader wanted to model the thermal explosion of RDX spheres dropped into a Woods metal bath at several hundreds of degrees Celsius. Merzhanov *et al.* studied the thermal explosion in cylindrical symmetry. Their findings are illustrated by the curves reproduced by Boggs & Derr (1990) in Figure 2.2.

The non-steady state (time dependent) solutions to the Frank Kamenetskii's Equations produce a series of time-dependent temperature distributions for each sub critical state whether the criticality condition is exceeded or not. In Figure 2.2 examples are shown of Merzhanov *et al.* (1963) studies. The families of curves have characteristics dependent on the Biot number. Hence, those temperature distribution profiles associated with solutions of the non-steady state equations where $Bi \rightarrow 0$ tend to be flattish whereas those associated with $Bi \rightarrow \infty$ tend to be significantly curved.

According to Lee (1998), the second influence on the shape of the time-dependent temperature profiled is the value of δ in relation to δ_{crit}, the Frank Kamenetskii Criticality Criterion, designated by "FK" in Figure 2.2.

We consider that there is a slight contradiction in the previous statement by Lee (1998), concerning the definitions of FK and δ, as this author previously

[3] According to STANAG 4240 (1991) Liquid Fuel Fire Tests for Munitions designates the large scale cook-off test by which an ordnance item is engulfed in the flame envelope of a liquid fuel fire, and the ordnance item's reaction is recorded as a function of time.

presented δ definition in a different way than FK defined by Boggs & Derr (1990), and at this stage into this explanation refers to the two entities as being the same.

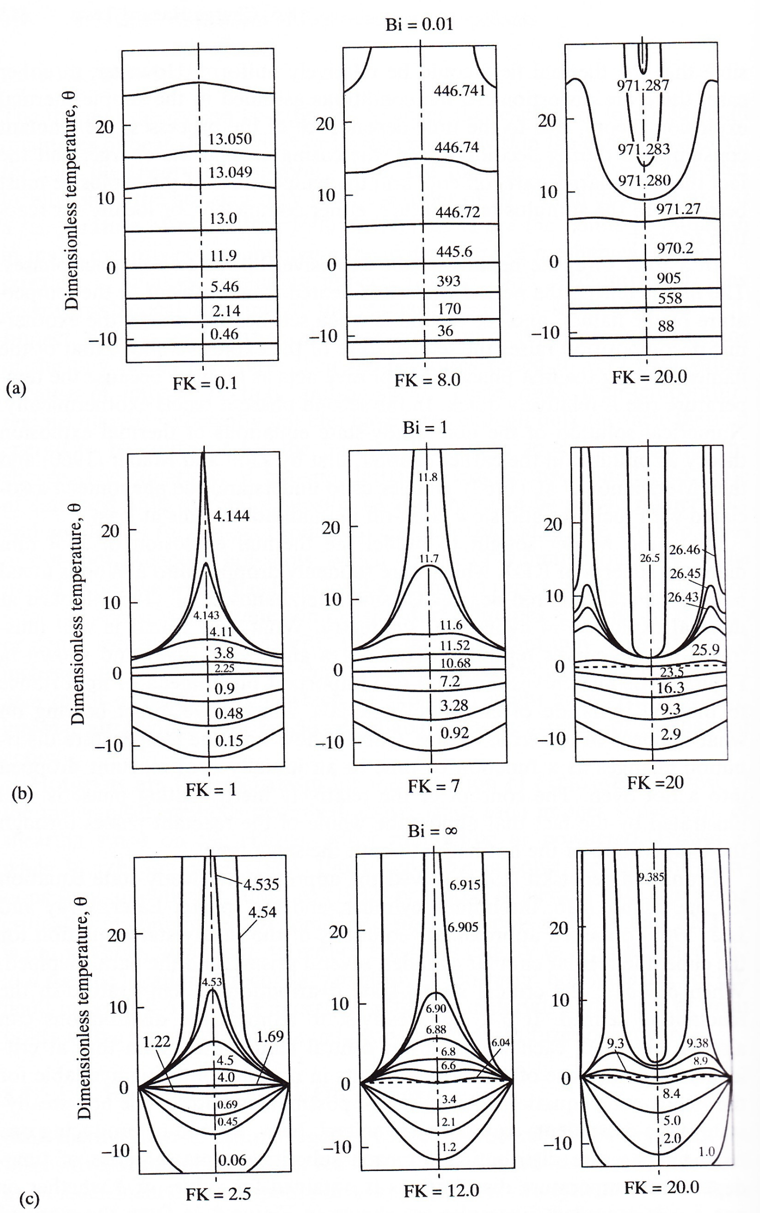

Figure 2.2 - Non-steady state temperature profiles for cylindrical reactants at various values of the Biot number and the Frank Kamenetskii's criticality criterion. (a) Non-steady temperature profiles at Bi = 0.01, for several values of dimensionless time t/t_{ad}. (b) Non-steady temperature profiles at Bi = 1, for several values of dimensionless time t/t_{ad}. (c) Non-steady temperature profiles at Bi = ∞, for several values of dimensionless time t/t_{ad}.

Nevertheless, Lee (1998) states that for situations where $\delta < \delta_{crit}$ (which for a cylinder is about 2), the steady state equations of heat conduction with distributed sources of heat can be solved to give steady state temperature distributions across the reactant, i.e., no explosion occurs - the system self-heats to give a peak central temperature, which then decays (Fig. 2.2).

If δ just exceeds δ_{crit}, the peak reaction temperature occurs in the centre of the reactant and the explosive explodes or inflames from the centre, more or less as an extension of the steady state theory.

Nevertheless, if δ exceeds δ_{crit} by successively larger amounts, the point of ignition gradually moves outward toward the surface of the reactant. In the limit case where $\delta >> \delta_{crit}$ ignition occurs at the surface of the reactant.

The importance of the profiles of Figure 2.2 resides precisely in the fact of allowing qualitative understanding of the Fast and Slow Cook-Off scenarios and why the results of the tests are in most of the cases so different.

The Slow Cook-Off scenario is presented by Figure 2.2 (a): the nearly uniform temperature in the reactant can be due to its high thermal conductivity or to a slow increase of the temperature of the environment. This would cause the wall of the reactant to increase slowly; therefore, the ignition is expected to take place at the centre of the reactant in a Slow Cook-Off scenario.

As for the Fast Cook-Off scenario, especially when an ordnance item with a thin highly conductive metal case is being tested, the major impediment to the heat transfer through the system is the low thermal conductivity of the reactant (explosive charge or propellant in the weapon) (Fig. 2.2 (c)).

One other aspect of this discussion being the degree in which δ exceeds δ_{crit}: in the case of Slow Cook-Off, δ is likely to exceed only very slightly δ_{crit}, therefore increasing the conditions consistent with a central type of ignition. In the cases of Fast Cook-Off or Fuel Fire, the criticality criterion is largely exceeded, due to the very high temperature to which the system is being exposed, and due to the fact that ambient temperature is expressed as a negative exponential thus having a significant effect on δ value. The ignition is, in this case, expected to occur near the surface of the system.

In the case of Slow Cook-Off the violence will be maximized, as the central initiation of the explosive will be augmenting any confinement effect to the ordnance item, while in the Fast Cook-Off the surface initiation will occur where confinement is only due to the case, which will soon rupture, therefore reducing even further any confinement to the system.

In either situation, the presence of a case induces a difference as it provides primarily confinement and also protection of the energetic material from the heat stimulus as well as defining the surface heat transfer coefficient between the system and the surroundings.

In any case, this qualitative understanding of the phenomena is a useful tool to indicate why most of the ordnance items tend to meet Fast Cook-Off or Fuel Fire requirements and not meet Slow Cook-Off ones.

2.2. FACTORS INFLUENCING COOK-OFF

The main factors influencing Cook-Off are chemistry, heating rate, confinement and sample dimensions (size and surface area/volume). Each of these parameters has a decisive role to play in the Cook-Off phenomenon, although the most important role is attributed to chemistry, as it is the very basis of all thermal degradation processes leading, or not, to a Cook-Off event.

A brief overview of the present lines of thought concerning the influence of these parameters on the Cook-Off phenomenon is given below, and leads to the conclusion that more experimental work is needed to understand the relative importance of these factors and the way in which they interact in different situations. So far, however, all the attempts to deal with these factors separately seem to have ended in failure.

Chemistry is undoubtedly the paramount factor governing the time and temperature at which a thermal runaway can start. This should be considered the governing parameter over the thermal degradation processes behind any type of Cook-Off event. Therefore, the understanding of the chemical mechanisms governing any Cook-Off process of the wide variety of energetic materials and their mixtures it is of fundamental importance. This aim does not yet seem to have been achieved.

Over the years many studies of thermal degradation processes have been performed on the widest possible range of pure materials and their mixtures under different conditions (temperature, pressure, atmosphere, moisture, etc.) and many explanations of the mechanisms leading to the experimental observations have been proposed. These explanations and the experimental results constitute a precious asset as they allow one to develop and apply modelling computer codes, which reduce the costs of predicting the occurrence of such violent events, increasing simultaneously the range of possible thermal scenarios tested in a very short length of time. However, in any real munition system, final proof will be made by a full scale trial.

Nevertheless, Belcher *et al.* (1991) state that although chemical kinetic studies worldwide have helped to identify the principal rate processes occurring in common energetic materials, uncertainties persist and a variety of kinetic mechanisms have been postulated. These authors also emphasize that temperature dependant material properties and phase changes add to the complexity of Cook-Off hazard assessment.

The reasons for our lack of understanding of the chemistry of these phenomena include the absence of direct diagnosis techniques for subsurface (condensed phase) or heterogeneous (gas-solid) processes during deflagration and no insight into species concentration profiles by sophisticated flame diagnostic techniques. Therefore, the present knowledge of the chemistry of ignition and combustion processes derives from indirect analytical sources as for example thermal degradation experiments or isothermal gas phase measurements. The interpretation of these experiments is normally far from simple and there might be several reasonable explanations of the same observable fact (Fifer, 1984).

Several reviews and experimental works have been published in the literature on thermal degradation of a wide range of energetic materials over the years, including Batten, Behrens, Brill, Chen, Cosgrove, Bulusu and respective collaborators, etc.. As these are outside of the scope of this study program they will not be reviewed here. However, brief mention will be made to some Cook-Off studies where the importance of the influence of chemistry on Cook-Off is clearly stated.

Ho *et al.* (1993) state that the development of satisfactory prediction methodologies and modelling tools requires the physico-mechanical and chemical kinetic properties to be known as a function of temperature, pressure and heating rate. They consider the heat of explosion of energetic materials to be one of the many factors governing Cook-Off response, but that the addition of plasticizers to propellant compositions decreases the level of violence of the Cook-Off response by a mechanism which is not well understood. They conducted thermomechanical properties studies and concluded that plasticizers are probably moderating the violence of Cook-Off response by decreasing the viscosity or increasing the flow of the material. Increasing the plasticizer level substantially increases the reaction time, but the initiation temperature is not necessarily altered. It is our opinion in this matter that the role played by the plasticizer is intrinsically related to the mechanical properties of the propellant, as the plasticizer acts by reducing the strength of the mechanical integrity of the propellant, thus reducing the opportunity for the reactions to grow.

These authors also concluded that the reaction time and temperature of propellants during Cook-Off are governed by the thermochemistry, such as thermal stability and decomposition kinetics: propellants with low thermal stability are easiest to ignite. Ammonium Nitrate (AN) based propellants produce very mild Cook-Off responses because its decomposition is endothermic.

Belcher *et al.* (1991) refer to experimental studies with ODTX apparatus, where increasing Nitrocellulose (NC) content in HMX formulations causes a dramatic decrease in time to explosion around 473 K - 523 K: a two-orders-of magnitude decrease over a 283 K temperature interval at 3% NC.

Fleming (1995) describes a discontinuity in the thermal behaviour of HMX/NC compositions at intermediate temperatures, becoming more pronounced as the proportion of NC is increased. He finds that at low temperatures NC decomposes exothermically first, but the HMX temperature is not sufficiently high to be strongly affected by the spike produced, and the time-to-explosion is only mildly influenced by the proportion of NC. At high temperatures, both HMX and NC react almost simultaneously and the time-to-explosion is independent of the proportion of NC. However, at intermediate temperatures, the HMX temperature is sufficient to promote rapid decomposition once the NC decomposes exothermically and a marked decrease in the time-to-explosion is observed.

According to Dagley *et al.* (1996), the Cook-Off response of pressed RDX-based PBXs (Plastic Binder eXplosives) is strongly influenced by the nature and level of a second explosive component, the particle size of the explosive crystals and the type of binder. Extensive studies performed with compositions containing one ethylene-vinyl acetate binder demonstrated substantial moderation of Fast Cook-Off response by blending low levels of TATB with RDX, or higher levels of TATB with finer RDX. The violence of Slow Cook-Off responses was decreased by the addition of PETN or TATB to RDX, but even higher levels of TATB did not reliably prevent compositions containing finer RDX from undergoing detonation reactions.

Parker & Dagley (1996) state that the high explosiveness of RDX generally leads to violent Cook-Off response in compositions containing relatively low levels (up to 5%) of binder or desensitiser. They identified several coating materials that can give a reduction in Cook-Off violence, at least at fast heating rates, and were examining these materials in conjunction with other explosives to effect further reduction of Cook-Off violence: both insensitive explosives which are Cook-Off resistant themselves (e.g. DATB, TATB), and more sensitive explosives (e.g. PETN) which may react at lower temperatures to cause charge disruption and release of confinement before the violent RDX Cook-Off reaction.

Confinement plays a major role in influencing the way in which a thermal degradation, which is invariably accompanied by a pressure rise, builds up into the subsequent event.

Farinaccio (1991) comments that the complexity of the Cook-Off mechanism is dependent on the degree of confinement and the mass of the explosive, and in his opinion, the ideal scenario for Cook-Off testing would include munitions of practical size and confinement subjected to a hazardous thermal environment.

Chidester *et al.* (1997) report that at low applied temperatures the ODTX anvils show relatively little damage and the calculations indicate that no thermal runaway occurs at these temperatures and the explosion results from the build up of thermal decomposition products. In munitions, the consequence would be a degree of damage dependent on the strength of the case and the effects are expected to be localised.

Heating Rate is another main factor influencing the Cook-Off event.

Farinaccio (1991) reports on an experimental study with known explosive mass contained in a generic munition casing specifically developed to determine the relationship between the heating rate and the reaction temperature of an explosive when subjected to various heating rates. The reported experimental observations indicate that time to Cook-Off increases for lower heating rates, and that reaction temperatures increase with increasing heating rates, for the same degree of confinement and sample dimensions.

Ho *et al.* (1993), in their studies of the kinetics of thermal decomposition of rocket propellants, found that increasing the heating rate did not alter the reaction order, but in general decreased the activation energy, i.e. the reaction mechanism was not altered but the decomposition rate increased. This suggests that in modelling Fast and Slow Cook-Off reactions it is important to determine the kinetic parameters at the appropriate heating rates. Furthermore, the same authors concluded that the heating rate and the propellant geometry determine the temperature distribution across the sample and therefore govern where the Cook-Off begins and consequently the violence of reaction.

Chin & Plooster (1994) report calculations of Cook-Off times, for different size explosive charges, that correlate in a linear fashion with heating rate. According to these authors, this is indicative that an explosive will have more time to generate enough heat to get a runaway reaction at the lower heating rate, and therefore the runaway reaction will start at a slightly lower wall temperature. Thus, independently of the size of the explosive charge, the time to deflagration or to detonation will be approximately proportional to the reciprocal of the heating rate.

Chidester *et al.* (1997) consider that in general larger scale Cook-Off tests have only qualitatively demonstrated the effects of heating rate and confinement strength on the violence of the resulting thermal explosion. They state that because most high explosives are large organic molecules with relatively low thermal conductivities and high heat capacities, rapid heating of an explosive to its decomposition temperature results in a relatively non-violent explosion, because only the outer edges of the explosive have been heated to any degree. A slow heating rate which allows the entire explosive charge to remain at an approximately uniform temperature prior to explosion results in a much more violent reaction that begins at or near the centre of the charge. The exothermic decomposition continues to produce hot, high pressure gaseous products until it is quenched (or at least slowed) by the failure of the confining medium. Therefore, they are of the opinion that the violence of the thermal explosion is determined by the external heating rate and also by the thermal diffusivity and chemical kinetics of the explosive, as well as the strength and inertia of the confinement.

Dimensions and Size of the Sample to be tested are also important parameters of the Cook-Off process. One of the major problems in Cook-Off is the scaling up of the tests, as the results obtained with larger samples (therefore larger surface area and volume) are not necessarily the same as the ones obtained with much reduced size samples.

Kent & Rat (1982) concluded that most of the Cook-Off experiments carried out in the U.S.A., especially in the course of applied studies in the field of auto propulsion, are designed to provide quick answers to concrete safety problems, and do not allow one to extrapolate.

Chin & Plooster (1994) investigated the influence of explosive charge size on Cook-Off times and heating rates. Calculations made for a cylindrical high explosive whose outer surface temperature is heated at constant temperature, demonstrated that in the absence of a self-heating term, the temperature as a function of time depends only on r/a^2, where r is a characteristic time for the process (e.g. time proportional to the inverse of the heating rate) and a is a characteristic length (e.g. the radius of a cylindrical or spherical explosive charge). According to the same authors, if the rate of heat conduction is the dominant process in Cook-Off testing, then double the radius of a cylindrical charge will require a Cook-Off time about four times as long to reach the same interior temperature profile for the same initial and boundary conditions. Thus to obtain comparable results in Slow Cook-Off tests with charges of the same shape but different sizes, the heating rate for the smaller charge should be greater by a factor of the charge radius squared than that for the larger charge. Results from calculations performed for different size charges at different rates are presented and demonstrate that the maximum heating rate corresponds to the minimum Cook-Off time and the minimum heating rate to the maximum Cook-Off time, and that Cook-Off times vary approximately with the square of the charge radius when the heating rates vary by the same factor.

They conclude from this numerical study that, in Slow Cook-Off situations, if one divides the Cook-Off times by the square of the charge radius, and multiplies the heating rates by the same factor, one observes that scaled Cook-Off times for smaller charges are slightly greater than for larger charges; larger charges have more time for reaction, therefore cook-off at lower wall temperatures than smaller charges.

Another factor considered important by its influence in the Cook-Off response is mentioned by Dagley *et al.* (1989): coating of explosive crystals. For example, coating the explosive crystals with polymer can help promote low response during

Cook-Off. However, poorly coated crystals, or those in which the coating suffers additional damage during pressing, do not show a comparable reduction, which suggests that the chemistry of these coatings is not significant.

2.3. COOK-OFF EXPERIMENTAL ASSESSMENT

The Cook-Off phenomenon has been assessed, with various heating rates often described as “fast” and “slow”, over the years at basically three types of scale which we call: super small (samples up to 0.02 kg), small (samples up to 0.70 kg) and large scale (or full scale, i.e. full sized weapon system). This is, however, not a formal definition of a ranking system for the scale in Cook-Off testing as not all the Cook-Off community subscribes to it. Also there is no universally agreed definition of “fast” and “slow” heating rates.

The development of Cook-Off tests has the sole purpose of gathering data that will provide the necessary insight into the Cook-Off phenomenon allowing further prediction of the response of explosive ordnance inadvertently heated during storage, transportation or handling.

An overview of the test facilities developed for Cook-Off assessment worldwide in the past decades is presented below, as a concentrated summary of widely scattered information, and to establish the background for the work in this thesis. For convenience, these are described by country, starting with the United States of America, as this was where the first Cook-Off programme was ever established following the dramatic consequences of the U.S. Forrestal accident in July 1967. Some general conclusions about the Cook-Off tests are presented at the end of the survey.

Firstly, however, we mention the various thermal analytical methods, which are commonly used to provide the information on the basic thermal properties of explosives necessary for an understanding of their Cook-Off behaviour.

2.3.1. Thermal Analysis

Thermal Analysis "is the general term for methods in which physical and chemical properties of a substance, a mixture of substances and/or reaction mixtures are measured as a function of temperature or time with the sample being subjected to a controlled temperature program" (Widman & Riesen, 1987).

Thermal analysis techniques are used to assess the thermal stability of any type of energetic materials, therefore allowing the gathering of thermodynamic and kinetic parameters from the components under study (e.g. activation energy, heat capacity and thermal conductivity, order of the decomposition reaction, etc.), that constitute essential input for any type of modelling codes being developed and/or utilised for cook-off prediction. The various techniques include: Thermogravimetry (TG), Differential Scanning Calorimetry (DSC), Adiabatic Rate Calorimetry (ARC) and the Heat Flow Calorimetry (HFC). These techniques typically use samples of a few milligrams.

Thermogravimetry (TG)

Thermogravimetry measures the weight loss of the material under study as a function of the temperature. Experiments are performed placing material on a sensitive balance, subjecting it to a heating programme in a pre-selected atmosphere, and recording all the weight variations induced (Widman & Riesen, 1987; Rooijers & Leeuw, 1987; Speyer, 1994).

Quantitative determination of the mass loss (or gain) can be related to the chemistry of the reaction, and can further be related to the heat changes detected using other thermal techniques.

Vaporization of reactants and/or products may cause problems.

Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry measures the power required to raise the temperature of a sample at a constant rate. Any variation in the thermal capacity of the sample, any phase change or any chemical reaction is registered as a change in the power input required.

DSC measurements are usually performed with a dynamic temperature program, which allows the scanning of a temperature range of interest, but may also be carried out isothermally. This thermal analytical technique allows the determination of specific heat, thermal effects, purity, polymorphism, glass transition, oxidative stability, chemical reactions, reactions kinetics, melting behaviour and crystallization, etc. (Widmann & Riesen, 1987).

Accelerating Rate Calorimetry (ARC)

This is perhaps the technique most descriptive of Cook-Off. A sample of material is held in a constant temperature enclosure and the sample temperature is monitored. If it remains constant the enclosure temperature is raised by a small amount. Eventually, a temperature is reached at which sample self-heating is detected. The rate at which the temperature rises can lead to predictions of thermal runaway.

Heat Flux Calorimetry (HFC)

This is a technique less applicable to Cook-Off than to the general study of the degradation of energetic materials at near room temperature and the prediction of their future life. The sample, which may be kilograms, is placed in an isothermal enclosure and the heat flowing from it is measured by very sensitive devices. Powers of microwatts or even nanowatts may be measured, so that reactions may be studied at temperatures resembling those for normal storage temperatures.

2.3.2. Cook-Off Testing Facilities

Many different Cook-Off tests have been devised in many different countries, and there is much international debate about the relationship between them, and about the validity of the various experimental processes and their relevance to real life. A brief review of the tests categorised by country follows.

United States of America

As a direct consequence of the catastrophic consequences resulting from two serious Cook-Off accidents on board the aircraft carriers, USS Oriskany (1966) and USS Forrestal (1967), the USA started a Weapon Cook-Off Improvement Program in the 1970’s (McQuaide, 1980).

At the Naval Weapons Center (NWC), Pakulak & Anderson (1980), Pakulak & Cragin (1983, 1986) and Pakulak (1984) reported on a Small Scale Cook-Off Bomb (SCB) built with the purpose of assessing the thermal behaviour of explosives with regard to Cook-Off time and temperature as well as the severity of response of Cook-Off reaction.

According to Helm & Hoffman (1994) and Hoffman & Helm (1995), the Small Scale Cook-Off Bomb was originally developed by Pakulak as a scaled down version of the DOD Fast and Slow Cook-Off tests, which are large scale Cook-Off tests required for main charge explosives, propellants and pyrotechnics qualification. This technique was extensively used by Pakulak and collaborators (Anderson & Pakulak, 1976 and 1978; Pakulak & Anderson, 1980; Pakulak & Cragin, 1983 and 1986; Pakulak, 1984; Pakulak & Clark, 1988) to evaluate the violence of thermal explosions in current explosives, to study possible mitigation techniques and to reduce costs in assessment of new thermally insensitive propellants and explosives.

Pakulak (1984) advocated that this technique could be used to assess the severity of the reaction by observation of both the SCB case and witness plate damage caused by the substance when subjected to external heating. Based on the deformation of the witness plate and the number of fragments obtained after the test, a scale of criteria (R-0 to R-10) was established to rank each test result as a burn, deflagration, explosion or detonation based on the degree of damage sustained by the test fixture:

- If no change in the vessel and no dent in the witness plate occurred then the Cook-Off reaction was classified as burning with a rating of zero (R-0);

- The maximum rating (R-10) was attributed to partial or complete detonation (many small pieces, hole, or almost punched hole in witness plate).

The term “dent” in the witness plate is associated, according to Helm & Hoffman (1994) and Hoffman & Helm (1995), with the explosive reaction of the substance causing the bottom plate to fly across the gap and leave an imprint rather than the buckling of the plate caused by expansion of the vessel.

Pakulak (1984) also suggested that the time-temperature profiles obtained could be used to establish if a substance met any of the thermal stability criteria.

The experimental set up for this technique comprises a steel vessel of 400 cm^3, and 3 mm thick walls, with two 400 W electric heaters fastened to the steel vessel, contains the sample (see Fig. 2.3).

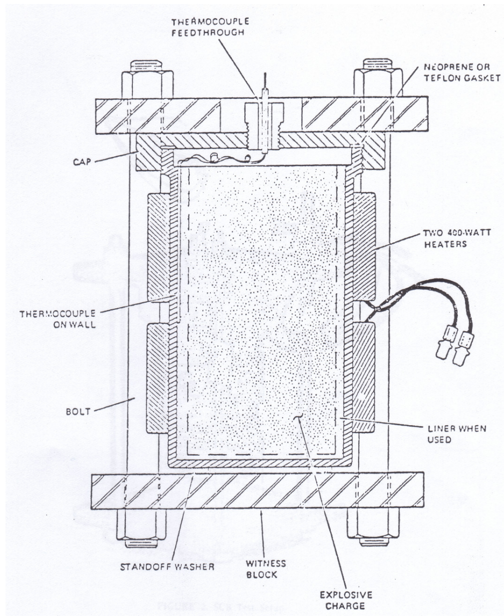

Figure 2.3 - Naval Weapons Center SCB Experimental Set-Up.

The vessel has a threaded steel cover with two feed-through fittings for thermocouple leads and for a pressure take-off. The mounting frame consists of two 135 mm by 12.7 mm steel witness plates with four 12.7 mm bolts that clamp the SCB vessel between them. The vessel is then instrumented with one or two plate-type thermocouples. If only one substance is being tested, a thermocouple is spot welded to the centre of the vessel wall. When two substances are tested, i.e., a liner material and an explosive material, a second thermocouple is used between the two substances. The plate-type thermocouples consist of a 0.3 mm thick Nichrome ribbon approximately 1 cm^2, with the thermocouple wires fanned out and individually spot welded to the Nichrome. The welder used should be designed for thermocouples welding, or should be a welder that is current-limited for use with small wire or thin metal. The choice for plate-type rather than bead-type thermocouples is related with the fact that the first give faster responses and more representative measurements of the temperature of the interfaces.

The author states that the substance of interest is loaded into the SCB steel vessel to within 10 mm (approximately) of the top, as the space remaining above allows for thermal expansion. The materials under study can be a solid, liquid, slurry, powder or gas under modified assembly and fill conditions.

The SCB unit is assembled and placed in a safety testing bay for remote firing, and it is heated by connecting the two electric heaters.

The heating rate normally used in these tests of 3 K/s is considered by Pakulak (1984) to be approximately that experienced by a high explosive (HE) fill in a heavy wall steel munition subjected to a fuel fire test, and 0.2 K/s is representative of that experienced by a HE fill in a thermally protected heavy wall steel munition subjected to a Fuel Fire. Anderson & Pakulak (1976) refer to a heating rate for Fast Cook-Off trials of 2.5 to 3 K/s. Helm & Hoffman (1994) and Hofmann & Helm (1995) report on a heating rate of 3 K/min with the Cook-Off tests following a thermal profile starting at 298 K until a reaction occurs or a temperature of 673 K is reached.

Boggs & Derr (1990) specifically state that after insertion of the test material the temperature is raised from 573 K at a rate of 3 K/min. This is in our opinion a very strange thermal profile, as a lot of energetic materials would have undergone Cook-Off before reaching a temperature of 573 K. Boggs & Derr (1990) present a table of typical results for the Small Scale Cook-Off Bomb Test and for Nitroguanidine (powder) the Cook-Off temperature presented is 20 K lower than the 573 K mention as starting point of the thermal profile. The authors indicate, however, that this test was performed with a higher heating rate of 1 K/s.

The temperature and time to Cook-Off are recorded by means of strip-chart recorders. The test is considered positive when test material has deformed in some way the witness plate, which forms the bottom of the testing vehicle, as a measurable dent is a strong indication that a detonation might develop if a larger sample was used (Pakulak, 1984; Rooijers & Leeuw, 1987; Boggs & Derr, 1990).

Pakulak (1984) suggested several criteria for positive tests for the U.N. Test Series depending on the type of material that is being tested.

This technique has been widely used by many other research groups all over the U.S.A. (Lawrence Livermore National Laboratory, Sandia National Laboratory, Crane Naval Surface Warfare Center, etc.) and the rest of the world (TNO-PML/Netherlands, DSTO/Australia, etc.) for assessing thermal response of numerous energetic materials under various heating rates and thermal profiles, due to its simplicity and flexibility to accommodate for any set-up changes to suit the different research projects (higher level of ullage, extra number of thermocouples, etc.).

At a later stage, the Small Scale Cook-Off Bomb was accepted and adopted as a test for classification of a substance as an explosive under the U.N. Hazard Classification of Explosives test procedures, the U.N. Orange Book "Transportation of Dangerous Goods" [4] - Test Series 1 and 2, as it simulates transport and storage situations involving slow external heating of a substance (Pakulak, 1984; Scholtes & van der Meer, 1994; Helm & Hoffman, 1994; Hoffman & Helm, 1995).

The acronym used to designate the Small Scale Cook-Off Bomb is generally SCB, but there are some authors that use instead the acronym SSCB to refer to the same experimental set up (e.g. Helm & Hoffman, 1994; Hoffman & Helm, 1995).

Generally SSCB refers to the Super Small Scale Cook-Off Bomb (SSCB) also built at the Naval Weapons Center, China Lake. This consists of a steel tube (28 mm external diameter, 23 mm inner diameter and 76 mm long) spot welded (in four points) to a witness plate (60 mm diameter and 10 mm thick). A similar top plate is bolted to the witness plate for explosive confinement. An internal aluminium sleeve (23 mm external diameter per 20 mm internal diameter), to spread the heat input evenly, and a thermocouple are placed inside the test vehicle. The explosive material is sampled (cast, pressed or cured) into two steel tubes (20 mm external diameter, 15 mm internal diameter and 32 mm long). Each tube contains approximately 0.01 kg of sample and two steel tubes are used per test. The outer tube is heated electrically by two 125 W heating bands. With 220 VAC applied, the heating rate is circa 1 K/min and approximately 0.2 K/min with 110 VAC. In this way time to Cook-Off, Cook-Off temperature (at a given heating rate) and severity of Cook-Off (by fragmentation of steel tube and witness plate) are assessed (Pakulak & Cragin, 1983; Boggs & Derr, 1990).

Chin & Plooster (1994) describe work performed on a Super Small Scale Cook-Off Bomb for surveillance of thermal hazards of stored munitions. The designed used is the same as Pakulak & Cragin (1983), with some changes: it is a smaller and simpler design accommodating the same quantity of explosive (0.03 kg), a smaller mass of metal which allows for better control of the temperature at the surface of the

[4] See "Recommendations of Transport of Dangerous Goods: Tests and Criteria", Second Edition, st/sg/ac.10/11/rev.1, United Nations, New York, 1990. According to the U.N. manual, the test simulates the transport, storage situations involving external heating and provides data for classification recording to test series 1(b)iii or 2(b)iv.

explosive charges, while simultaneously reducing the effective degree of confinement of the explosives (see Fig. 2.4).

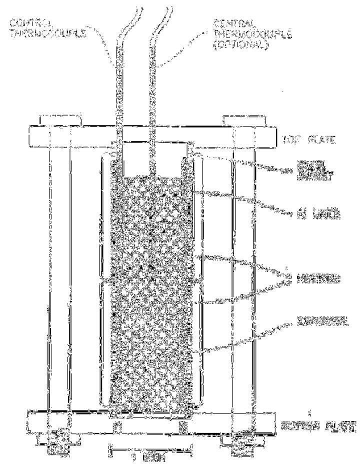

Figure 2.4 - Modified Super Small Scale Cook-Off Bomb.

The authors report on scaled up version of this test vessel by a factor of two with a charge weight of 0.28 kg.

This test was instrumented far more extensively than any comparable small scale test (see Fig. 2.5):

- type K thermocouples arrays with ground noise loop maintained by using isolated thermocouple probes and differential input signal conditioning;

- face-on piezo resistive pressure gauge to measure the blast pressure arising from the explosives reaction. Measures to minimise noise from vibrational and/or electrical standpoint, and thermal pulse created by the test item were employed;

- fibre optic light sensors and solar cell light sensor system to detect the intensity and duration of total light emitted when the cook-off bomb case ruptured;

- velocity screens to measure the velocity of fragments from the cook-off bomb.

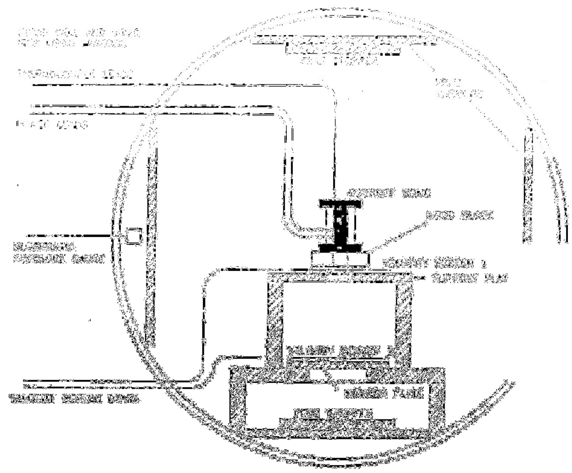

Figure 2.5 - Modified Super Small Scale Cook-Off Bomb Experimental Set-Up.

The thermal profile consisted of an initial fast ramp up to a temperature of 373 K, a soak period of 10 minutes for the small charge and 45 minutes for the large one, and then a steady ramp at the selected heating rate until Cook-Off occurred.

Time to explosion was measured considering the overall time of the pre-selected thermal profile, i.e., sum of the fast heating ramp up to 373 K, soak time and second heating ramp until Cook-Off occurs.

The authors consider, on the basis of the results obtained, that SSCB can be used to simulate the Cook-Off of a larger or even full scale device, if proper measuring devices, such as solar light sensor and velocity screens, are used.

A discrepancy was noted in the total mass of the sample indicated by Chin & Plooster (1994) - 0.03 kg - and Pakulak & Cragin (1983) and Boggs & Derr (1990) - 0.02 kg - for this SSCB technique.

Anderson & Pakulak (1976) described Slow Cook-Off studies on Amatex-20K in an oven consisting of heavy walled aluminium tubing with a welded base plate. Heating elements were attached to the outside of the tubing and controlled from a thermocouple imbedded in the aluminium wall. The ovens were covered with heavy aluminium foil to minimise evaporation and sublimation of the sample. The ovens and samples were heated rapidly to the chosen temperature and controlled at that temperature until cook-off occurred. Two sample sizes were tested: one with 5.08 mm in diameter and 15.24 mm in length and another with 13.33 mm in diameter and 20.32

mm in length. The temperature of the thermocouple located at the exact centre of the charge and on the inside wall at the explosive/aluminium interface was continuously recorded. A third thermocouple was placed at a half-radius point in the larger samples to monitor the temperature distribution on the sample. Time to Cook-Off data are presented as equivalent time to Cook-Off calculated as time at the oven temperature corrected for the amount of reaction that occurred during the warm up period.

The Toaster Oven Slow Cook-Off Technique was initially implemented at the Naval Weapons Center, as it became apparent that very little was known regarding the changes that occur within propellants as a function of time during a Slow Cook-Off process. The first SCV tests were implemented to provide insight and empirical data regarding propellants behaviour as a function of temperature and were conducted with cylindrical propellant samples contained in Pyrex graduated cylinders that were heated at 25 K/h in modified household toaster ovens while physical changes, as a function of the temperature, were observed with a video camera (Boggs & Derr, 1990).

According to Boggs & Derr (1990) the current SCV tests provide the following data:

- bulk volume change of the propellant as a function of time;
- visible physical changes as a function of temperature;
- the radial thermal profile through the propellant with temperature and time;
- the oven air temperature and the temperatures and thermal profile within the propellant sample at the time of auto ignition;
- sometimes location of the auto ignition can be observed;
- the composition and volume of gases given off by the heated propellant as a function of temperature and time, which is useful for predicting the degradation characteristics in a full scale motor that will cause various problems common to propellants in motors: grain collapse, exudation of propellant through the nozzle, etc.. Also information on the physical state and degree of confinement can provide information on violence of response from propellants in a rocket motor. Data from SCV tests can also be used to estimate time to reaction and Cook-Off temperatures on full scale motors. SCV test results can be also used as aid tools in the design and retrofit operations as changes in the propellant formulation can affect propellant

behaviour during Slow Cook-Off and can be obtained by conducting matrixes of Cook-Off tests with one ingredient at the time.

The SCV experimental apparatus comprises a custom-designed 304.8 mm long Pyrex graduated cylinder that accommodates a 50.8 mm in diameter and 45.72 mm long propellant sample (see Fig. 2.6). The Pyrex graduated cylinder has parallel red and white markings spaced 3.17 mm apart that can be easily observed by a video camera against a light or dark coloured background. Eight thermocouples are integrated into the base of the Pyrex cylinder and extend into the propellant sample: two are placed close to the inside walls, three are at half radius, and three adjacent to the vertical centreline of the propellant sample. The thermocouples at the wall are 180 degrees apart and lie on the horizontal centre plane of the propellant sample. The three thermocouples at the half radius and the ones in the centre are spaced 120 degrees apart at three heights (1/4h, 1/2h, and 3/4h) to form a three dimensional space arrangement.

The thermocouples used in this study were 3.17 mm in diameter bare stainless steel thermocouples probes. There is ongoing discussion about the use of non-metallic temperature sensors (glass or ceramic coated stainless steel thermocouple probes, as there is the argument that metallic probes will catalyse propellant decomposition by direct contact with the heated propellant) and the benefits of using probes with reduced dimensions (less displacement of propellant, conduction of less heat in and out of the sample, more accurate positioning in the sample).

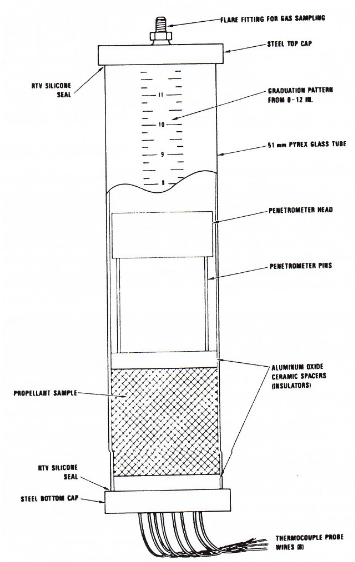

Figure 2.6 - NWC SCV Slow Cook-Off Technique.

The SCV apparatus is then introduced in a heating chamber (see Fig. 2.7).

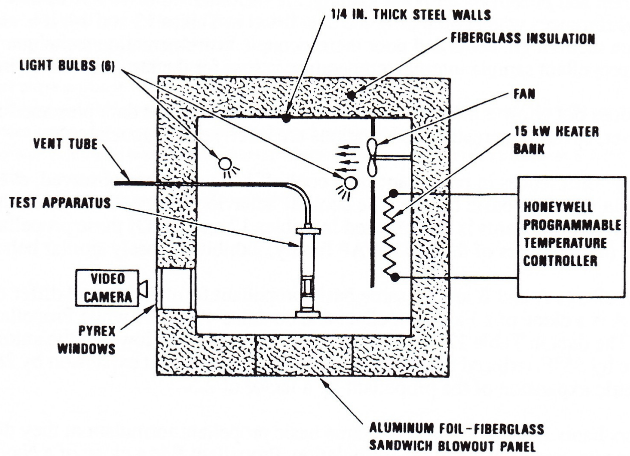

Figure 2.7 - NWC SCV Heating Chamber.

The thermal profile used in the tests was selected to give a complete cycle not exceeding a working day: during the first hour the test item is heated at a linear rate to a predetermined preheat temperature, followed by a ramp at 13.9 K/h until auto ignition of the sample occurs. The preheat temperature and ramp rates were calculated to give a maximum duration of the test of 7 to 9 hours.

According to Boggs & Derr (1990), the subscale propellant samples are heated at 13.9 K/h in an attempt to approximate thermal profile similitude with the bulk propellant in a typical full scale rocket motor heated at 3.3 K/h. This, however, is not a consensual matter, but according to the authors no changes to the adopted heating profile scheme seem necessary at this time.

The test instrumentation consists of twelve temperature sensors, blast overpressure gauges within the chamber volume, and continuous video coverage.

The differences between the results registered with the "Toaster Oven" and the SCV techniques are: sample size and penetrometer point loading (see Fig. 2.6). Furthermore, it is also important to point out that thermal gradients and poor thermocouple instrumentation technique yielded unreliable maximum propellant sample internal temperature values for the tests conducted in the "Toaster Oven".

The O(ne) D(imensional) T(ime to) (e)X(plosion) Test was developed at the Lawrence Livermore National Laboratory, as a well controlled, heavily confined environment to assess the time to explosion at confinement pressures up to 150 MPa. The ODTX apparatus consists of two aluminium anvils, which are machined to accept either slabs or spheres (see Fig. 2.8). The first can be electrically heated from 373 K up to 673 K, with the temperature being maintained within 0.2 K. The anvils are held together under a hydraulic pressure of 20.7 MPa, which allows for a confinement cavity pressure of 331.2 MPa. Pressure values exceeding 331.2 MPa from an explosive event will breach the cavity confinement. The anvils hold an explosive sample of circa 2 x 10^{-3} kg in the shape of a 12.7 mm diameter sphere. The induction time is defined as the time elapse from closure of the anvils till the rupture of confinement, e.g. occurrence of an explosion (Rooijers & Leeuw, 1987; Boggs & Derr, 1990; De Graauw, 1998; Tran *et al.*, 2001).

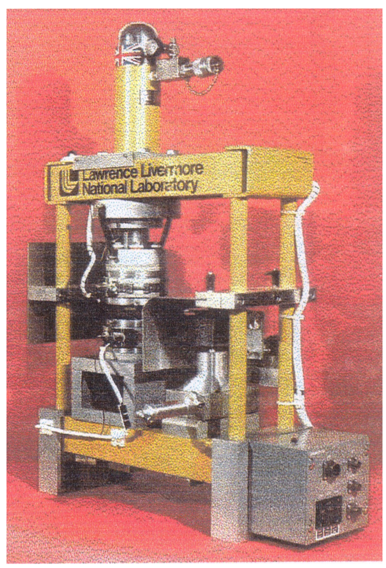

Figure 2.8 - ODTX Experimental Set-Up.

The main function of this facility is to provide the time until an explosion occurs in a controlled temperature and confinement environment. The tests were performed with high explosives like TATB, TNT and Plastic Bonded Explosives containing RDX and HMX. The typical temperatures were found within the range 400 - 650 K and the times to explosion range from a few seconds to about one day. The results obtained with this facility have been successfully compared with theoretical calculations using computer codes developed at the same research facility (Rooijers & Leeuw, 1987; Boggs & Derr, 1990).

Tran *et al.* (2001) provide a very detailed description of an upgrade incorporating new components, modern equipment and expanded diagnostics including in-situ temperature sensing and control, faster sample loading, external (hydraulic) pressure sensor, and computer controlled operation and data collection capabilities, in which the basic design parameters such as sample size, materials and dimensions of anvils remain unchanged for comparison purposes with previous work. These improvements allow very accurate determination of the temperature and the time to explosion, which is needed to investigate effects of parameters as sample heterogeneity, impurity and confinement pressure on the decomposition kinetics.

Tests conducted with TNT to verify the performance of the new ODTX apparatus are described.

Fisher & Benham (1993) developed a One-Dimensional Cook-Off-Confinement experiment that automatically controls the thermal history while massive lateral confinement allows quantification of the violence of the reaction through pressure, strain, and piston-velocity measurements. The apparatus was modelled intentionally to ensure that the heat flow was as close to one dimensional as possible. Up to 0.02 kg of energetic material is heated until a piston assembly fractures and the piston is driven up the barrel of this experimental set up. The quasi-static and dynamic pressures produced by the sample are measured with pressure transducers. The strain on the fracture web of the piston assembly is also measured. When the piston assembly fractures, the velocity of the portion travelling up the barrel is measured with a VISAR (Velocity Interferometric System for Any Reflector). In Figure 2.9 a schematic representation is shown.

The piston assembly, barrel, chamber and base are made of 4340 steel. The barrel liner is also of 4340 steel and allows the barrel to be refitted if the piston movement damages the barrel liner. The heating system comprises heat tapes wrapped around this experimental arrangement. As heating is supplied to this arrangement, the sample is being heated by conduction through the steel and sample cup.

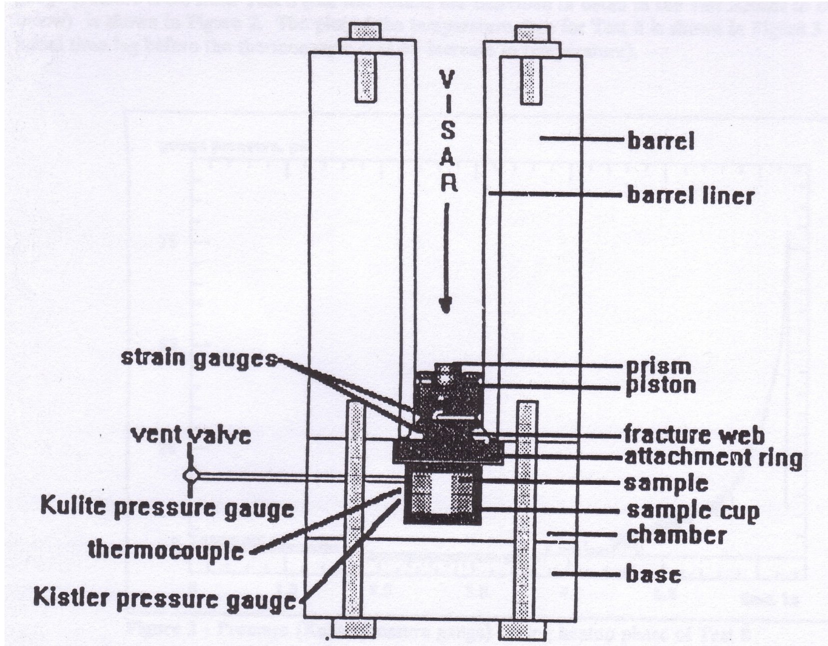

Figure 2.9 - Cook-Off - Confinement Experimental Set-Up.

The sample cup is made of Vespel (a low thermal conductivity high temperature polyimide) used to keep most of the thermal gradient in the sample cup and make the temperature across the sample essentially constant. The sample can be introduced as a poured powder or as a pressed sample.

The piston assembly includes the piston, the fracture web and attachment ring. The piston is kept in place by a fracture web designed to break when the pressure in the sample volume exceeds a threshold value. The fracture web is made by machining a groove on the exterior diameter of the piston and a channel from the bottom up as far as the top of the groove. The fracture web was 0.381 mm thick for the Cook-Off tests performed. The piston assembly helps to minimise the free volume within the sample cup while obtaining a quick rupture of the sample confinement when the pressure threshold is reached. Gases are contained during the heat up phase until the piston breaks. After the fracture web rupture, the inner portion of the piston travels up the barrel. Photometric coverage shows that gases, preceding the piston due to leakage as it travel up the barrel are negligible.

The instrumentation used for diagnostics (vent tube, pressure transducers, and thermocouples) was installed by means of mechanical feedthroughs, designed to contain gases and minimise added volume. The vent tube, plugged with a rod so that additional free volume is minimal, extends about 127 mm to a quasi-static Kullite model XT-190-500A strain gauge type pressure transducer and a vent valve. The Kullite transducer measures the slow changes in pressure during the heat up phase of the experiment. The data is displayed by a Workbench PC on a PC screen and recorded at a rate of 1 Hz.

The vent valve was placed to vent any pressure generated during an experiment in case of a misfire, i.e. the piston does not rupture and travel out of the barrel. So far the barrel functioned correctly and there was no need for the vent valve.

A thermocouple is inserted in the sample cup by means of a drilled hole to within 5.08 mm of the sample cup. The temperature measured is used to control the heating rate.

Two strain gauges are attached to the fracture web on the piston. The strain is displayed and recorded during the heat up phase of the test by Strawberry Tree software.

When the piston moves in the beginning of the rapid reaction process, the pressure in the sample volume, the strain on the fracture web, and the velocity of the piston are recorded. The breaking of a looped optical fibre generates the trigger for the dynamic data acquisition with HeNe laser light passing through it. The fibre loop is passed through the side of the barrel and barrel liner with a mechanical feedthrough, such that the loop is within 0.508 mm of the top of the piston. When the piston begins to move, the loop is broken and the loss of return light causes a trigger to be generated and a fiducial marker to be recorded.

According to the authors, this fiducial is generated with precision adequate to correlate the pressure, strain, and velocity traces in time. The fiducial is identified as time zero in the dynamic data.

The dynamic pressure is measured with a 1 μs response time Kistler quartz transducer inserted into the chamber. The front face of the transducer is positioned 5.08 mm from the Vespel sample cup according to Kistler specifications. One hundred holes, 0.762 mm in diameter, are drilled in the sample cup to allow the pressure to be communicated to the transducer. The sampling rate for data recording is 1 MHz. The same sampling rate is used to record the strain on the fracture web when the piston starts to move. The strain gauges break before the piston has fractured and becomes free to travel up the barrel. The dynamic strain records provide information about the early part of the response of the energetic material.

The piston velocity as it travels up the barrel is measured with a VISAR. A corner cube prism is mounted on top of the piston to reflect enough light for the VISAR measurement. The piston is reported to have been successfully tracked in most tests as it travelled up and exited the barrel.

The pressure, strain, and velocity measurements are related and characterize the violence of reaction.

Circumstances beyond our control prevented us from accessing Gibson (1991) and Alexander *et al.* (1994a and 1994b) publications referring the U.S. Navy Variable Confinement Cook-Off Test (VCCT). Other publications on this equipment were made available to us: Baer *et al.* (1996) depicted Cook-Off testing by means of a the U.S. Navy Variable Confinement Cook-Off Test (VCCT), developed at the Naval Surface Warfare Center as an explosive screening test, in assisting the development of predictive Cook-Off models towards assessing the violence of reaction during Cook-Off of confined energetic materials.

These authors describe the VCCT experimental set as consisting of a cylindrical geometry which confines the energetic material with an aluminium sleeve and a variable thickness steel sleeve. Steel witness plates at either end provide axial confinement and washers are used to centre the energetic materials between the plates. The test vessel is closed by means of bolts. Heater bands located in the outside of the steel confinement sleeve provide the heating. In a typical VCCT Slow Cook-Off test the temperature is quickly ramped at 373 K in 1 hour and then the confinement is thermally soaked for 2 hours at that temperature. The heating rate is then 3.3 K/h until ignition. A heat transfer analysis of Slow Cook-Off test with HMX, in these heating conditions, is presented and thermal ignition is predicted to occur when the temperature at the aluminium sleeve reaches ~ 463 K and the location of the thermal runaway takes place at the centre of the HMX at a time of 30h 27m, in agreement with experimental data.

Schmitt & Baer (1997) report that the VCCT heating bands extend approximately 80% around the circumference of the steel sleeve.

Maienschein & Nichols III (1997) described the test fixture as consisting of two end steel plates and a variable thickness steel tube. Inside the steel tube there is an aluminium tube, which helps distribute the heat uniformly within the device. A cylinder of energetic material is placed between two sets of steel washers, whose purpose is to place the explosive within the uniform heating region. The washers have a hole in the middle that also provides some space for thermal expansion. After an initial ramp, the temperature is raised at 3.3 K/h. The experiment continues until the confinement bursts. An experimental sequence will vary the thickness of the exterior sleeve and characterize the violence of response as a function of confinement.

Sandusky *et al.* (1998) reported Cook-Off studies performed in a VCCT to evaluate the threshold and violence of reaction in PBX-9502 when subjected to a standard Slow Cook-Off test. In this study the higher confinement version of the VCCT with 19 mm thick end plates with a maximum 3 mm thickness for the steel confinement sleeve is used, but the standard VCCT is described.

According to these authors, in normal VCCT, the thickness of the steel confinement sleeve is varied from 0.4 to 3.0 mm to obtain a threshold of violent reaction from slow heating at a rate of 3.3 K/h (see Fig. 2.10). There is also an aluminium sleeve of 1.5 mm thickness inside the steel sleeve.

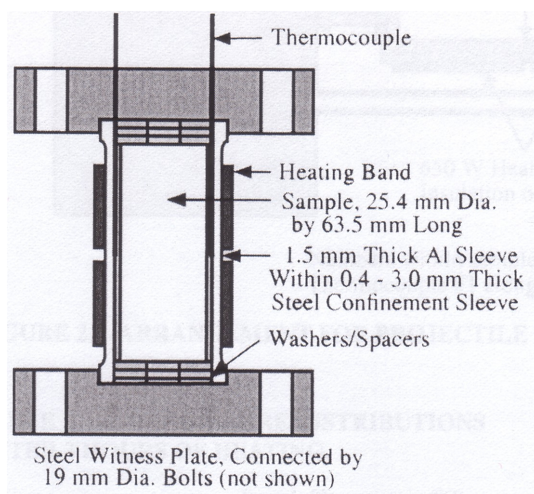

Figure 2.10 - NSWC Variable Confinement Cook-Off Test.

The temperature can be ramp at any desired rate and dwelling periods are also possible.

The authors refer thermal profiles involving the following steps: temperature ramp from room temperature to 523 K in 2 hours, dwelling period of another 2 hours and then ramp at 3.3 K/h until an event occurred.

Temperature measurements are made by means of two thermocouples inserted in the space between the steel and the aluminium sleeves at half height of the cylinder.

Baer *et al.* (1998) stated that VCCT attempts to categorize the level of reaction violence based on an average fragment size of the confinement case material after it has failed. The same authors are of the opinion that this only yields qualitative information on the strain rate behaviour of the confined material, and do not provide a mechanistic understanding of Cook-Off of the energetic material.

In a VCCT Cook-Off test, the level of violence is assessed by *post mortem* analysis of the test apparatus. A level of violence is based upon size and number of fragments of the confinement. Accordingly, increasingly violent events are classified as burn, pressure rupture, deflagration, explosion, partial detonation, and detonation. The distinction between these categories is entirely subjective.

Atwood *et al.* (1999) state clearly that testing of the PS propellants in the VCCT device and numerical studies at Lawrence Livermore and Sandia National Laboratories have indicated that there are design issues (lack of confinement, gaps, and lack of diagnostics) that limit the VCCT applicability for providing the data needed for quantitative comparison. Design improvements have focused on better sample confinement and diagnostics at an acceptable cost. The most promising design is a 25.4 mm diameter cylinder of energetic material confined in a mild steel tube 50.8 mm in length, with an internal diameter of 20.32 mm, sealed with copper end plugs held in place by a vise (see Fig. 2.11).

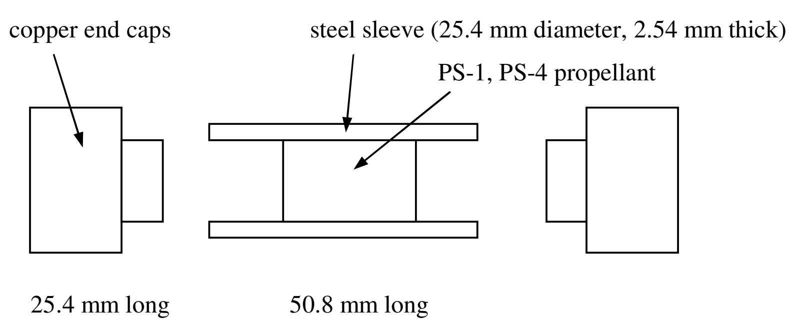

Figure 2.11 - NAWC Small Scale Cook-Off Device.

Because the thermal expansion of the copper is greater than the steel, as the device is heated the end caps expand at a greater rate than the steel providing increased sealing of the tube.

Preliminary experiments using AP/Al/HTPB propellants PS-1 and PS-4 at heating rates of 1, 5 and 10 K/min were reported. According to the authors, it appears that for these materials the adequate confinement was achieved. Thermocouples were located at the centre of the sample tube (controller) and at the centre and edge of one of the end plugs. Wall velocities were determined by means of flash X-ray data. The authors advocate that further studies on a sample of material with a known history of extreme Cook-Off reaction violence are needed to verify the utility of this experiment.

Melof & Olson (1997) described the Violence of Cook-Off Reaction apparatus (VOCR) which has been developed at the Research Center for Energetic Materials at New Mexico Tech. This apparatus consisted of a sample chamber and an outer, concentric aluminium heat sink fitted with electrical band heaters. A pneumatic cylinder allowed remote insertion of samples into the heated sample chamber. A pressure port was bored into the sample chamber and a piezo electric pressure transducer (pressures up to 3.45 MPa sampled at 2 kHz) was connected via 3.17 mm tubing. The tubing served as a thermal standoff and prevented overheating of the pressure transducer. The weighed samples were consolidated into a thin-walled aluminium blasting cap shell (6.5 mm I.D. x 7 mm O.D. x 41 mm length) sealed by pressing a machined aluminium plug on top of the loaded material and introduced into the pre-heated apparatus (see Fig. 2.12).

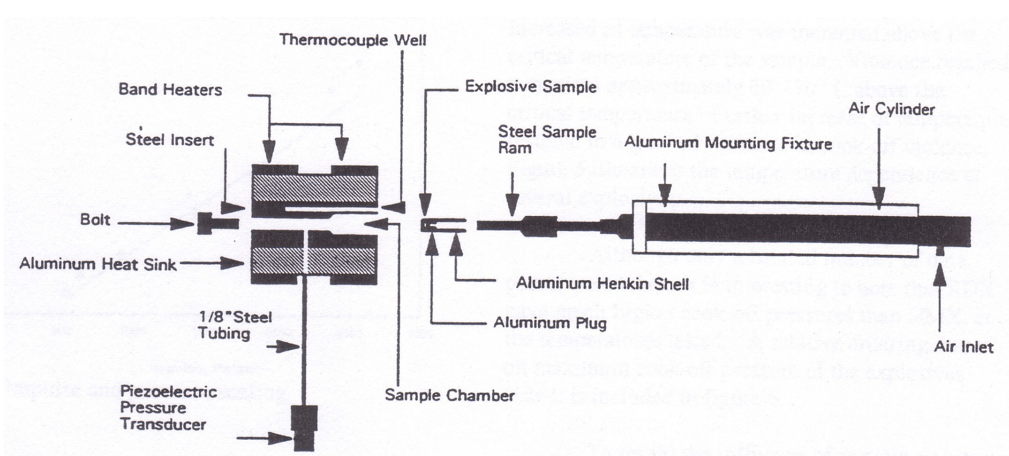

Figure 2.12 - Violence of Cook-Off Reaction (VOCR) Apparatus.

Time to explosion, peak pressure and total impulse were determined for each test. Exploded sample shells were ejected by removing the rear bolt and pushing the spent shells from the sample chamber with a bronze rod.

The authors state that small sample sizes give results to highly scattered results due to small, random, difficult to control variations in sample geometry. The geometry variations caused thermal runaway to begin at a slightly different location in every sample. The location at which thermal runaway began influenced the maximum pressure obtained. In larger samples, geometry variations have less of an effect, therefore 20 x 10^{-6} kg was the smallest sample tested. Further tests were performed with 40 x 10^{-6} kg samples.

Peak pressure was directly measured and total impulse was calculated for each pressure profile. As peak pressure is easy to obtain, it was selected as the violence indicator.

Chidester *et al.* (1997) describe a device for measuring the violence of response of a hollow explosive cylinder. The geometry of the hollow explosive cylinder, the surrounding confinement, the heater bands, and the velocity timing pins is shown in Figure 2.13. Each hollow explosive cylinder had an inner radius of 29.3 mm and an outer radius of 76.2 mm, was 224.9 mm long, and weighed approximately 6.6 kg. In the heavily confined tests, 2 cm thick steel cylinders were placed outside of 5 mm thick aluminium cylinders, which were used for better heat distribution into the explosive. In the lightly confined tests, only the 5 mm thick aluminium cylinders were used. In one test, an intermediate cylindrical confinement of 5 mm aluminium and 6 mm of steel was used. Aluminium, steel, tantalum, and brass inner cylinders 3.2 mm thick, were used to vary the impedance on the inside of the charge.

External velocity timing pins were placed at distances varying from 17.0 to 34.0 mm every 120° around the charges. Internal velocity timing pins were placed 1.7, 3.7 and 6.7 mm from the inner cylinders every 120° to measure the collapse velocities of the inner cylinders. The solid explosive charges were 74.9 mm radius by 224.9 mm long cylinders weighing approximately 7.7 kg. The four large external heating bands shown supplied most or all of the heat to the explosive, whereas two smaller ElectroFlex heater strips, which ran the entire length of the inner cylinders, were used to attain nearly isothermal conditions in the hollow experiments with slow heating rates.

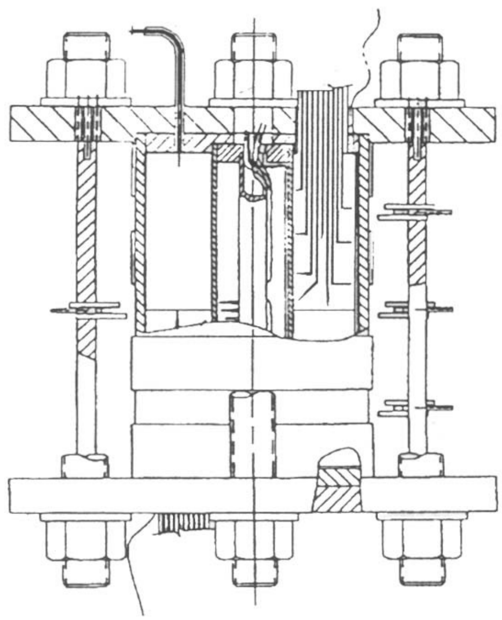

Figure 2.13 - Hollow Thermal Explosion Experimental Configuration.

The heat flow into HMX- and TATB-based explosives, the time to and location of the resultant thermal explosion, the resulting internal pressures and the acceleration of the metal confinement cylinders were measured. It was shown that fast heating rates produced less violent events than slow heating rates because only the outer layers of explosive contribute initially.

At the Naval Surface Weapons Center, White Oak, Maryland, a Fast Cook-Off test facility was assembled to assess the Thermal Detonability of explosive boosters and main charge explosives. The experimental set-up consists of a fire pan filled with standard JP-5 jet fuel and a Cook-Off bomb containing the explosive to be studied. The bomb consists of a 38 mm long tube with a 25 mm internal diameter closed with two pipe caps and fitted with a thermocouple attached to the inner surface of the bomb. The explosive charge, 25 mm diameter and 25 mm long, is placed in the tube. After ignition of the fuel, a record is made of the time profile of the temperature rise, the Cook-Off temperature and the effect of the Cook-Off event on the bomb. One should note that the temperature reported here is that of the bomb inner surface/explosive surface interface. The temperature increase in the bomb inner surface is usually between 313 K/min and 323 K/min. It is also possible to determine the temperature at Cook-Off point vs. heating rate. The severity of reaction involves five different levels considered for this test: mild burning, mild pressure rupture, violent pressure rupture, partial detonation and high order detonation (Rooijers & Leeuw, 1987; Boggs & Derr, 1990).

A Large Scale Slow Cook-Off facility was assembled at the Naval Weapons Center as a standard U.S. test based on DOD-STD-2105A (Navy, Draft, 1989), in which the item is preheated to 328.5 K and the air surrounding the test item is heated at a rate of 3.3 K/hour until reaction occurs. The temperature is monitored throughout the test by several thermocouples. The possibility of thermocouples being placed internally to the motor exists. One should note that this test is normally performed with motor nozzle covers securely in place.

Any other devices that allow better visualisation or insight to the phenomenon such as internal video camera, steel witness plates, blast overpressure measuring system, etc., have been incorporated into this facility.

This large scale facility is not an equivalent of any particular operational scenario, but it allows one to determine the case-liner interface temperature when reaction occurs, as one of the requirements was (prior to I.M. policy) that no reaction occurred until the case-liner interface exceeded 422 K (Boggs & Derr, 1990).

A Slow Cook-Off study is reported by von Holtz *et al.* (1993) conducted on a toroidal composite vessel containing 6.5 kg of RX-08-FK Paste Extrudable Explosive (see Fig. 2.14). Two tests were conducted: first, where the end pieces were adhesively bonded into place without set screws and second, in which the composite vessel end pieces were secured in place with setscrews.

Ten strain gauges and five thermocouples located at various points around the toroid were used to provide data. Additional instrumentation consisted of two video cameras.

The thermal profile used consisted of 3.3 K/h after an initial 8 h soak period at 347 K.

This test was design as part of the development of the Paste Extrudable Explosives (PEX) Main Charge transfer system being developed at Lawrence

Livermore and Sandia National Laboratories. The test was design to provide information on at both system and products levels.

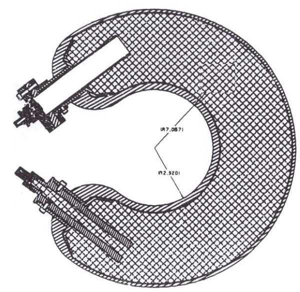

Figure 2.14 - Toroid Composite Vessel in its Post-Fill Configuration for Slow Cook-Off Test.

The procedures for the Slow Cook-Off test were the ones defined in MIL-STD-2105A. The PEX filled vessel was mounted on an aluminium stand and placed in an oven, whose internal dimensions were approximately 122 mm x 122 mm x 122 mm. The oven, on its shipping pallet, was placed in a plywood stand, which elevated the oven 80 mm above the ground (see Fig. 2.15).

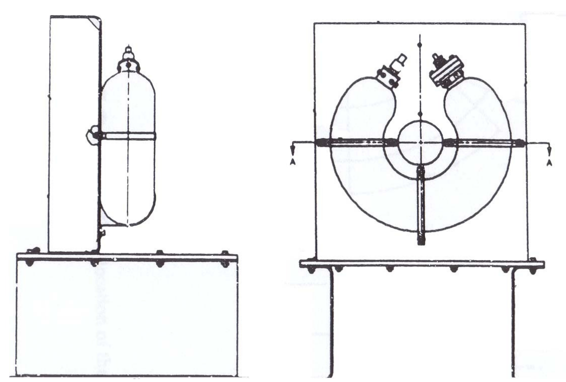

Figure 2.15 - Slow Cook-Off Test Assembly, including Toroid Composite Vessel and Stand.

The vessel was instrumented with 13 strain gauges and 5 thermocouples, located at various points of the toroid. Assessment of the violence of reaction was made based on a *post mortem* analysis.

Smith (1972) reports on ordnance response to massive jet Fuel Fires. These were some of the very early Fuel Fire tests developed immediately following the USS Forrestal accident. The Fuel Fire tests described involve the suspension of the ordnance item to be tested in its pre-launch configuration above the test site surface dependent on the height of the ordnance above the flight deck when racked to an aircraft, usually 914.4 mm and 1676.4 mm. The test site was constructed to contain both the water to provide a level fuel surface and the jet aircraft fuel, which provided the fire energy source.

According to the author, two types of test sites were used:

- a test pan which was constructed on the ground surface by building an earthen retaining wall (304.8 mm height x 304.8 mm width). Polyethylene or steel plate was used to provide a watertight bottom. This test site was suitable for tests with winds up to ~ 10 m/s, not a very common condition at Dahlgren except in the very early hours of morning.

- a test pit (152.4 mm thick steel plate and approximately 3048 mm deep) was constructed to alleviate this problem. Pipes imbedded in the banks assisted in providing oxygen to the fire.

The minimum and maximum sizes for the test sites were 640 cm^2 and 1120 cm^2, respectively.

Complete time to event histories were recorded for each test. Thermocouples placed between the ordnance case and explosive load monitored the internal temperature profiles of the ordnance as a function of time. Pressure measurements of the ordnance blast overpressure were performed with piezo electric gauges.

Visual records of the events were made by means of CCTV and motion picture cameras.

Minimum test specifications were a 30 s time interval for fire build up a flame temperature of 811 K, and a minimum average flame temperature of 1172 K until an event takes place.

Presently the Fuel Fire Test is considered an example of a large scale Fast Cook-Off test facility. What started as a standard U.S.A. test based on DOD-STD-2105 (Navy, 1982) and MIL-STD-1648 (AS) (1982) is now a Standard NATO Agreement under the designation STANAG 4240. This test consists of engulfing a test item in the flame envelope of a liquid Fuel Fire and recording its reaction as a function of time.

In this test the item to be tested is suspended horizontally above the surface of a pit filled with any of the considered suitable liquid hydrocarbon fuels (JP-4, JP-5, Jet A-1, AVCAT or commercial kerosene Class 2). The distance of the test item from the pit should be such that it satisfies the following temperature requirements: the flame temperature shall reach 823 K within 30 s after ignition of the pit as measured by any two of four flame thermocouples. The flame temperature is measured by four thermocouples (with time constants of 0.1 s or less) located outside the ordnance skin. An average flame temperature of at least 1143 K as measured by all valid thermocouples at the test item without contribution of the burning ordnance will be considered a valid test (Boggs & Derr, 1990).

United Kingdom

The Cook-Off work developed in the U.K. has always followed the U.S.A. trends, up to the present date where international policy on classification and hazards testing results normally from research work developed under cooperation protocols.

Several studies have been conducted specifically on Cook-Off of ammunition in hot guns.

Emmott *et al.* (1971), at R.A.R.D.E., report Cook-Off work on the evaluation of medium calibre munitions in hot guns. The effect of heating various 30 mm shells in expendable ovens at different temperatures for various periods of time was studied.

Some earlier studies, mentioned by these authors, on the effects of heating small explosive charges under confinement lead to the conclusion that the dimensions of the explosive charge, the precise conditions of confinement and the assembly were of paramount importance, therefore the need of obtaining data concerning fuzed and unfuzed Service stores. For this purpose, small expendable ovens were developed to heat shells and allow for the measurement of time-temperature profiles.

According to Emmott *et al.* (1971), the ovens were designed to be destructible, and were made from 457 mm diameter and 610 mm length aluminium tube, accommodating samples sizes up to 120 mm shell. A standard 2 kW copper sheated pyrotenax heating cable (58 m length) was wound around the outer surface of the tube.

The tube was closed at one end with a 12.7 mm thick “Sindanyo” insulation board, and at the other end with a similar board containing a simple door or shutter arrangement (sees Fig. 2.16).

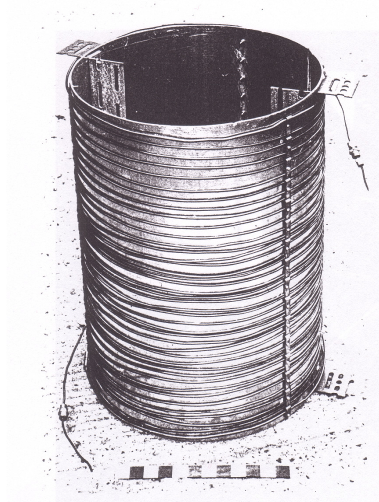

Figure 2.16 - The Basic Oven for R.A.R.D.E. Cook-Off Tests.

The heaters were covered by fibre glass wool to provide insulation and the heater complete was arranged on “dexion” framework. Further “dexion” framework was used to hold the door or shutter in position, and a sliding device extending from outside the heater, through the door into the heater was also provided. By a simple arrangement of wires and pulleys a sample could be drawn into the heated oven and the oven could be operated by remote methods (see Fig. 2.17).

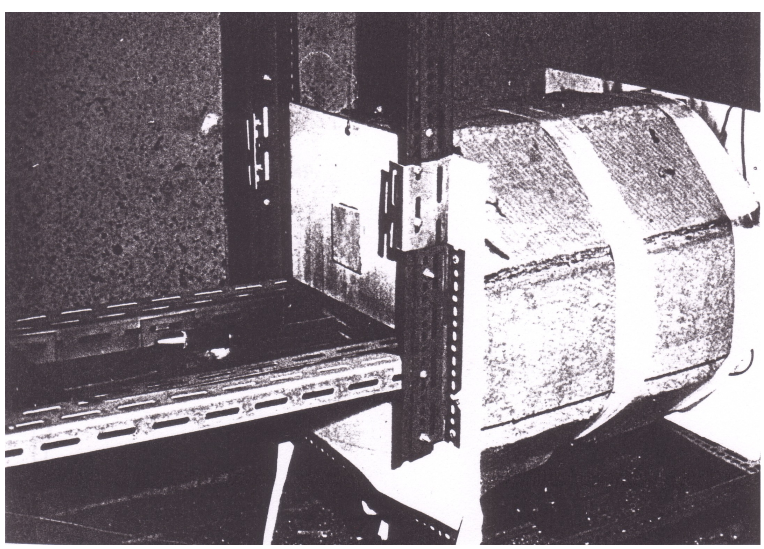

Figure 2.17 - Complete Oven Unit for the R.A.R.D.E. Cook-Off Tests.

The sample was contained in an oven at a selected constant temperature for periods up to 6 hours unless there was a prior explosive event. The range of temperatures used was 413 - 473 K. The oven (air) and shell skin temperatures were recorded continuously for each test and a time/skin temperature profile was obtained for each shell at each predetermined oven temperature.

Cottle *et al.* (1974) report work on Cook-Off of bare charges of RDX and RDX/PU suspended in heated enclosures, Slow Cook-Off of artillery projectiles both in disposable ovens and in heated sections of gun barrels, at R.A.R.D.E. as well. These experiments were intended as to provide information concerning the likelihood of explosion from projectiles stuck in heated gun barrels.

After these first studies into gun prematures, a Small Scale Burning Tube Test was developed in R.A.R.D.E.. Hubbard & Lee (1978) describe experiments performed in such devices in order to assess explosiveness of high explosive fillings and propellants. Propellant charges were placed in a mild steel tube (254 mm length with an external diameter of 44 mm), with a 6 mm thick wall. The closure of the tube was made by means of two screw on end caps. The length of the explosive charges used was reduced in order to accommodate for a 12 mm air gap at one end of the charge. In the earlier experiments ignition was achieved by means of a hot wire, but in this study a small propellant/fuzehead system was used at the end with an air gap. Time to event was measured.

In this same series of tests other parameters were evaluated: scaling and confinement effects.

A Large Burning Tube with a 9 kg capacity, overall length 711 mm, I.D. 102 mm, O.D. 127 mm of mild steel with heavy mild steel end caps, was used to assess the effects of scaling up. Ignition was again by a propellant/fuzehead system set in a cast or machine pocket of 20 mm in diameter and 5 mm deep in one end of the charge.

As for the confinement study the only dimension varied in relation to the standard Small Burning Tube was the wall thickness: 1.6 mm. This created a difficulty: the thickness of the metal was too small to cut screw threads and therefore no screw-on end caps could be placed. The adopted solution was to achieve confinement by holding the end caps in placed by the opposed faces of the R.A.R.D.E. version of the Picatinny Arsenal set back simulator. Time to event was measured.

Another series of tests is also reported: small burning tubes in Fuel Fires. The small burning tubes were suspended horizontally above the initial surface of 1 x 10^{-3} m^3 of petrol burning in a metal bucket. Times to explosion were recorded and the fragments of the ensuing event collected.

Hutchinson & Connor (1982) also report on studies performed with R.A.R.D.E. Small Scale Burning Tube in Fuel Fire trials to examine the effect that varying the length and radius of explosive charge has on the type of explosive event produced. Three different internal diameters were selected 25 mm, 31.4 mm and 40 mm and for all cases the wall thickness was kept constant at 6 mm. After filling these vessels with explosive of density 1.6 Mgm^{-3}, the weight of the charges was approximately 0.200, 0.315 and 0.510 kg, respectively.

The test assembly involved suspending the tubes circa 110 - 120 mm above the surface of a square tray containing 2 x 10^{-3} m^3 of petrol. Once this had been ignited, the time to Cook-Off was measured. Tests were performed with no thermocouples (see Fig. 2.18).

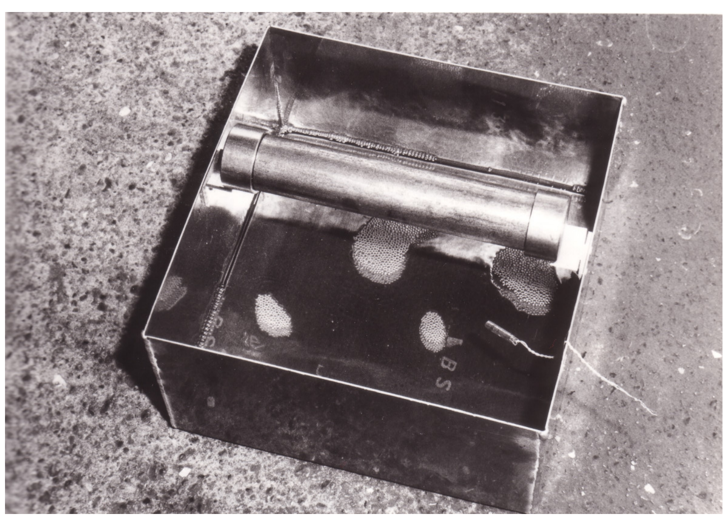

Figure 2.18 - Experimental Arrangement for the R.A.R.D.E. Small Scale Fuel Fire Test.

Hutchinson & Connor (1983) present an overview on the development of the Small Scale Burning Tube, for the purpose of determining hazards posed by the thermal ignition of moderately confined explosives in munitions and it is the authors' conviction that this set up provides also valuable information concerning the potential hazards of larger, but less strongly confined charges as found in many types of conventional warheads. This test has been used for several purposes: to rationalise and understand accidents, as a tool to assist explosives designers to assess the potential hazards of new formulations, and as part of the qualification testing required by the Ordnance Board before they can be advised on safety and suitability for Service of new compositions (see as an example Ordnance Board Proceeding 42746 (1991)).

One of the historical details worth mentioning at this stage is that initially the configuration of this set up involved a series of holes drilled along the tube to allow for deflagration or combustion velocities to be estimated by observing the first appearance of reaction products at each hole as a function of time after ignition by means of high speed cinematography. The idea was soon abandoned as the holes weakened the tube and strongly influenced the confinement.

Another weakness of this same configuration was the use of internally threaded end plugs, which failed at relatively low internal pressure, with consequent release of confinement, and posed a hazard due to the possibility of explosive being trapped in the threads, which could lead to initiation during assembly. The solution adopted involved screw on end caps.

Several points of serious discussion arose: the level of confinement achieved, in order to realistic assess the violence of response, the number of tests to carry out to have meaningful results, and the costs of testing. The recommendations from the authors for implementation standard procedures for testing and reporting data, creation of comprehensive database for comparison with future results, are the very important issue at this stage in this type of experimental study.

Hutchinson (1985) describes a R.A.R.D.E. Small Scale Booster Cook-Off Test, where the configuration previously presented is instrumented with 0.5 mm thermocouples fitted to monitor the temperature at the centre of the explosive charge and at the centre of the inside wall. This assembly when completely confined has a bursting pressure in excess of 0.18 GPa. The test is carried out above (110 - 120 mm) the same 2 x 10^{-3} m^3 petrol contained in an open square tray of side 300 mm, and the fuel is ignited electrically. The author refers a special insulation (woven carbon fabric) to minimise heat transfer down the steel sheath to the thermocouples.

This author describes another technique to measure time to explosion: Critical Temperature Test. For this test, the experimental configuration was selected to reproduce a booster housing assembly: a 25 mm diameter by 25 mm long explosive sample was encased in an aluminium alloy container with 3 mm thick walls. Steel sheathed 0.5 mm in diameter thermocouples were potted into the centre of the charge and at the centre of the inside wall (see Fig. 2.19). The vessel has a bursting strength in excess of 40 MPa. The sample is lowered remotely into a heated bath of liquid paraffin or silicone oil (depending upon the selected temperature), the temperature of which was maintained at + 273.5 K by heating tapes and constant stirring of the medium with nitrogen gas.

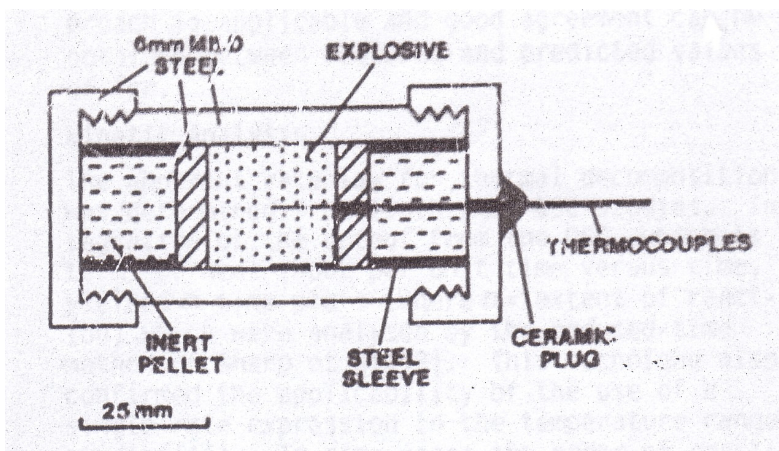

Figure 2.19 - Experimental Arrangement for the R.A.R.D.E. Critical Temperature Test.

The temperature of the centre and wall of the charge was monitored until either there was evidence of an explosion entirely disrupting the test sample, a rapid change of the centre temperature indicating that a pressure burst had occurred or the slow, exothermic decomposition associated with ambient temperatures below the critical value had ceased. The time to explosion plots were constructed based on the time intervals between the entire sample reaching the preset bath temperature and an event occurring.

Another test to be considered is the R.A.R.D.E. Temperature of Ignition Test, which has been nominated for the AOP-7 tests manual (1988). It is possible to test all types of explosive systems. The experimental set-up consists of a standard glass test tube (100 mm long, 12 mm external diameter), containing 2 x 10^{-4} kg of the sample, which is inserted into a metal block, externally insulated and heated at 5 K/min (see Fig. 2.20). All the information related to the event is then recorded. In this apparatus a variable heating rate is an advantage (Boggs & Derr, 1990).

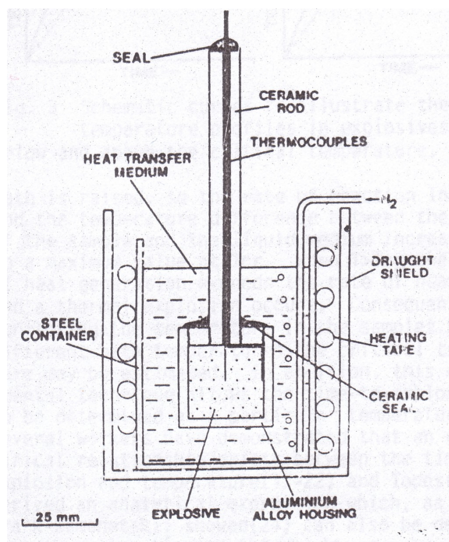

Figure 2.20 - R.A.R.D.E. Temperature of Ignition Test.

R.A.R.D.E. also developed Large Scaled Vessel Test (LSV), which was nominated for AOP-7 test manual (1982). In this test (heated type), the sample is sealed in a 2 x 10^{-3} m^3 seamless steel tubing standard vessel (internal diameter of 76 mm and 95.2 mm external diameter) with welded end-plugs 450 mm apart. The heating is achieved through a nickel-chrome heating wire around the tube and current applied in order to obtain 5 K/min, the process being monitored by a thermocouple inside the vessel and in thermal contact with its inner face through its housing. The violence of the response is assessed by the degree of fragmentation presented by the test vehicle (Boggs & Derr, 1990).

Slow Cook-Off testing for all types of explosive stores is assessed in the United Kingdom by placing the item under trial in a disposal metal jacket, which is cylindrical and built in halves that are bolted together after the store is put in. There is a significant space for air circulation around the sample. The ends of the jacket are attached to flexible hoses for air circulation; when the air circulation is closed the whole air-duct construction is heavily insulated in order to conserve energy. The air heater and pump are kept separated from the jacketed store by a reinforced concrete wall. A thermocouple monitors the air temperature inside the jacket half way along the length of the store, controlling the heat flux from the heater to the circulating air to maintain the rate of the temperature increase according to the preset program: 3.3 K/min. The number of thermocouples may vary up to five in order to monitor the temperature in several locations within the store or at its surface. In case of a malfunction of any type during the trials or if the maximum temperature programmed has been reached without an event occurring, a demolition charge on a remotely controlled trolley is provided to be used (Boggs & Derr, 1990).

Belcher *et al.* (1991) and De Graauw (1998) report experimental work on a One-Dimensional Time-to-eXplosion apparatus, designed at Lawrence Livermore National Laboratory. Modelling the obtained results was the aim of the first mentioned authors, and the latter implemented this technique at the Royal Military College of Science/Cranfield University, producing an operating manual and a risk analysis, and, simultaneously, studied the mechanisms and activation energies of PETN.

An experimental study on gun prematures was also developed by Anderson (1997) by means of a Bofors 40 mm/70-calibre gun barrel. Temperature and time profiles were obtained.

Cook-off studies have also been used in the U.K. as an assessment tool to design thermally insensitive plastic bonded main charge explosives (e.g., Hutchinson, 1985; Totterdell & Hutchinson, 1988).

France

Experimental work on Cook-Off has been undertaken at Société National des Poudres et Explosifs (S.N.P.E.) - Centre de Recherches du Bouchet, France, since 1981 by Kent & Rat. The experimental facility consists of a steel cylindrical combustion chamber with a 20 mm wall thickness, an internal diameter of 80 mm and depth of 600 mm (see Fig. 2.21). Three resistance heaters can electrically heat this enclosure up to 673 K. This set-up was used for propellant samples up to 0.20 kg and 50 mm of diameter. A thermocouple was fitted along the cylinder axis right to the centre of gravity of the sample, which was then introduced into the preheated combustion chamber. The induction time to a combustion event, and the temperature history of the propellant are measured by means of continuous recording systems. The impossibility of gas tight closing of the combustion chamber, so that total confinement is obtained, is a major disadvantage of this facility (Kent & Rat, 1982; Rooijers & Leeuw, 1987; Boggs & Derr, 1990).

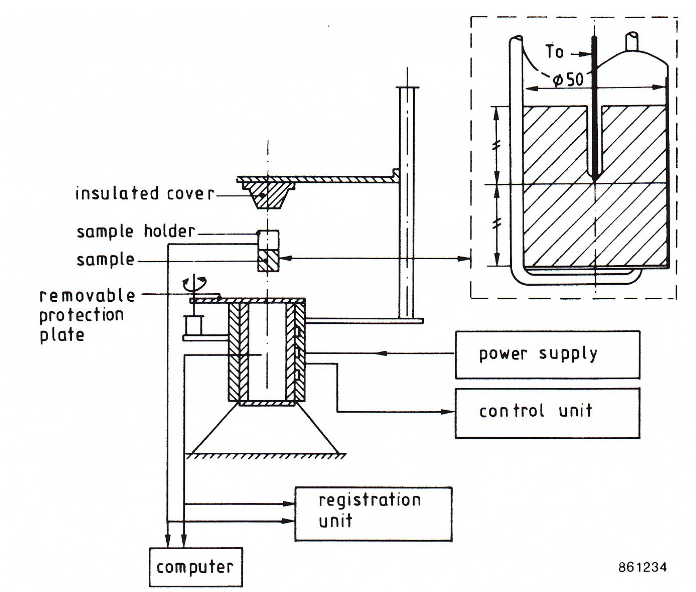

Figure 2.21 - SNPE Test Experimental Set-Up.

Kent & Rat (1982) undertook experimental work on three types of composite propellants and three types of double base propellants. Reported experimental results show that the critical temperature is typically 450 K and the induction time can be up to 18 hours (Kent & Rat, 1982; Rooijers & Leeuw, 1987; Boggs & Derr, 1990). These results were used in a computer code developed by Casenave & Racimor (1984) to predict time and critical temperature to Cook-Off. Several geometries were considered and a good correlation between experimental and theoretical results was obtained (Rooijers & Leeuw, 1987; Boggs & Derr, 1990).

Large Scale Slow Cook-off tests are also performed at S.N.P.E. using a Solid Propellant Vulnerability Test - 3L Rocket Motor Model (see Fig. 2.22). The motor, instrumented with thermocouples, is inserted in an oven at a heating rate of 3.33 K/hour, and the temperature at which an event occurs and the severity of the event are determined (Boggs & Derr, 1990).

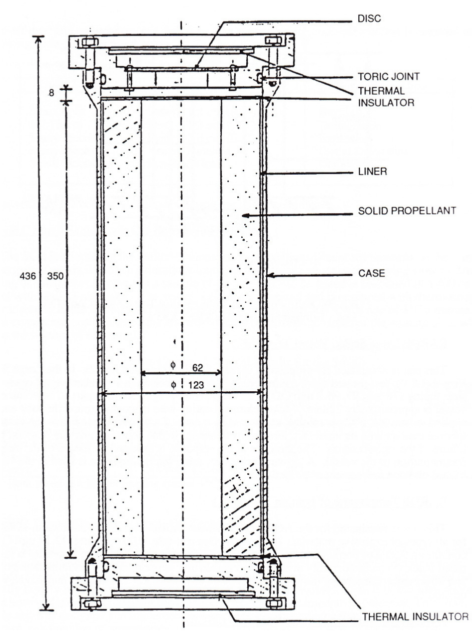

Figure 2.22 - Solid Propellant Vulnerability Test - 3L Rocket Motor Model.

Guengant *et al.* (1999) reported on the Unconfined Thermo-Ignition Test, a Slow Cook-Off test developed 20 years ago, in which a sample, 50 mm in diameter by 50 mm height, is heated in a constant oven temperature until reaction. The maximum “critical temperature” is measured by a thermocouple, i.e., the maximum constant temperature which never leads to ignition in such geometry. Parameters are calculated and the authors claim prediction of thermo-ignition delays with accuracy better than 2% for Slow Cook-Off tests and a database of more than 500 compositions has been established.

These authors also reported on the Under Confinement Pyrolysis Test, being developed, that is carried out in similar fashion except for the smaller dimensions of the sample (25 mm diameter by 25 mm height) and the fact that the sample is submitted to a pressure increase up 10 MPa, that allows determination of the “critical temperature”, i.e., maximum constant temperature which never leads to pressure increase.

Tests performed by the Groupe d’Études et Recherches de Pyrotechnie (GERPy), focussed mainly on the auto-ignition of single base propellants. In this case, samples of pressed cylindrical (3 to 11 mm in diameter with a radius/length ratio of 1:6) propellant charges, fitted with thermocouples, are introduced in an oven at constant temperature. Thus, it is possible to determine the temperature profile and the induction time to Cook-Off. Once again, there is good agreement between the experimental results and the calculated ones (Rooijers & Leeuw, 1987; Boggs & Derr, 1990).

Two other publications from Lemoine *et al.* (1994), from the Commissariat à l’Energie Atomique - Centre d’Etudes du Ripault, present a study on Slow Cook-Off in strongly confined granular explosives. This study has been conducted on a laboratory test apparatus modified to analyse the effects of different parameters: reactive and physical parameters, micro structural characteristics, applied temperature profiles (ramps with various heating rates, temperature thresholds) and confinement strength. This set up includes a uniaxial press and a mould. The upper part of the press includes gauges and hydraulic units, while the lower part comprises the heating system and a safety container that limits the extension of the pyrotechnics effects. Both parts are separated by a strong hard steel plate protection. The test chamber is a 10 mm hole in the mould that carries a sample up to 2 x 10^{-3} kg. The mould bottom ruptures at static pressures of 400 MPa. The maximum temperature is 773 K. Different measuring devices are implemented on this apparatus to allow data collection on (see Fig. 2.23):

- decomposition gases pressure inside the chamber;

- mould bottom velocity after mould break up;
- light emission produced by reaction;
- applied temperature;
- piston displacement.

The mechanical damage to the mould and the test chamber strains are measured after the test.

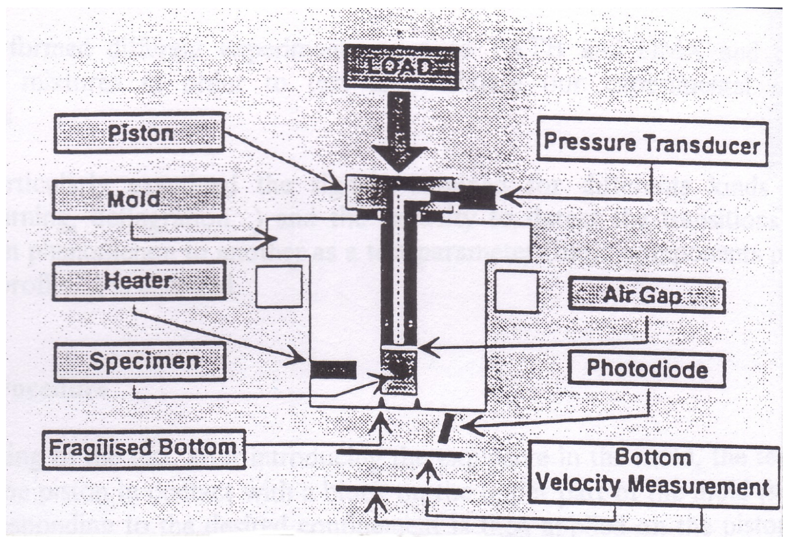

Figure 2.23 - Centre d'Etudes du Ripault - Experimental Set Up.

Four descriptors are used to describe the violence of response:

- Pyrolysis - slow pressure rise, mould break up for a pressure of 400 MPa, low bottom projection velocity of ~ 200 m/s, no light emission, weak chamber damage;

- Burning - same effects with an additional long light emission (several milliseconds);

- Deflagration - dynamic effects are observed if deflagration is obtained by transition from combustion: compressive or shock waves, high pressure rise above the static rupture value before the bottom is projected to significant higher velocity than previously (~ 700 m/s), light emission observed as for burning;

- Detonation: the previous effects are significantly amplified and the mould suffers higher level of damage.

The tests reported were performed with TATB, HMX and TATB/HMX mixtures, with a maximum static confinement of 400 MPa and a heating rate of

8 K/min. An air gap of 1 mm was maintained in all tests between the bottom of the piston and the sample surface.

These tests validated the capability of this set up to identify the type of reactions produced and the critical test parameters for which transitions from one reaction type to another are obtained.

Belgium

Similar tests were performed at the É(cole) R(oyale) M(ilitaire), Belgium, by Erneux *et al.* (1983), as their facility can be considered a smaller version of the S.N.P.E. test set-up, the main differences being the sample size (only 2 x 10^{-4} to 2 x 10^{-3} kg were used) and that Cook-Off under confinement studies were performed as well. For the sample size studied, a good correlation was obtained between experimental and theoretical results (Rooijers & Leeuw, 1987; Boggs & Derr, 1990).

The Netherlands

Pasman (1967) described a method to predict the induction period of thermal explosions by measuring the heat production as a function of temperature over the range 250 - 470 K. This method has been developed at TNO Prins Maurits Laboratory, and is presently known as Adiabatic Storage Test (AST). In AST, the time profile of heat generated by reacting species, under approximately adiabatic conditions, is measured. The experimental set-up used at TNO Prins Maurits Laboratory consists of a 1.5 x 10^{-3} m^3 Dewar vessel sealed with an insulated stainless steel lid, which can be flushed with gas pre-equilibrated at the temperature of the sample to minimise heat losses. The vessel is placed in an oven kept at the same temperature as the sample in the Dewar vessel. Thus, the heat developed in the sample is entirely used to increase the sample's temperature. An internal electric heating coil is used to set the sample at the desired initial temperature as well as to determine the heat capacity of the sample (see Fig. 2.24).

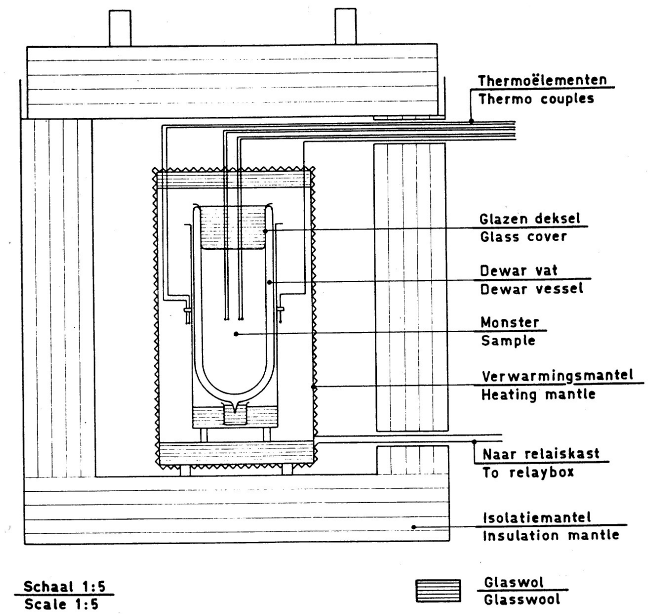

Figure 2.24 - Adiabatic Storage Test Experimental Apparatus.

Monitoring the sample temperature allows the determination of the heat generation. If the heating rate is significantly fast the experiment is stopped. The smallest detectable amount of heat is in this case 15 mW kg^{-1} (Pasman, 1967; Rooijers & Leeuw, 1987).

The Dutch Thermal Step Test (TST) allows high temperature kinetic studies of energetic materials decomposition. Samples are confined in a capillary stainless steel tube (internal fixed diameter of 1 mm and variable external diameter by a 70 mm length), which is part of an electrical circuit. The discharge of a capacitor raises the tube temperature to 300 - 1400 K within approximately 30 μs. Temperatures up to 1000 K can be maintained for several hours. The induction time is considered to be the time to the rupture of the tube and is measured over a range of wall temperatures. Studies have been performed in a significant range of materials and, for low temperatures, the tested propellants and explosives present a pseudo first order Arrhenius type of decomposition. This facility has allowed gathering a significant list of activation energies for energetic materials (Rooijers & Leeuw, 1987).

In the TNO - Prins Maurits Laboratory, a Small Scale Cook-Off Bomb has been also built with the purpose of assessing the severity of response of energetic materials to Cook-Off. This device was built according with the test series 1 and 2 of the UN Orange Book (Rooijers & Leeuw, 1987; Scholtes & Makkus, 1993). There is a slight difference in relation to Pakulak (1984) described technique, on the locations of the thermocouples, as the second thermocouple is placed in the centre of the substance to be tested. The heating rate used is 3 K/min. The test is started at 298 ± 3 K and until a reaction occurs or a temperature of 673 K is reached.

This test was intended not only as a contribution to TNO's research program, but as a contribution to the harmonisation of the tests recommended by the United Nations. However, on the construction of the equipment it became obvious that the U.N. Orange Book did not specify the details of the equipment and the experimental procedure sufficiently well to allow the experiments to be repeated adequately. Nevertheless, the project developers believe that this test, after minor corrections, can be used for classification of explosive compounds in test series 1 and 2 (Scholtes & Makkus, 1993).

Further development of this test facility (Scholtes & van der Meer, 1994) led to conclude that some design parameters such as thermocouple and heater positions, stability of the voltage and stand-off washers have an influence on the reproducibility of the temperature measurements and consequently on the test results. Additionally, tests with several unconfined materials showed very poor reproducibility; therefore it was decided to perform all future tests with confined materials only. From these experimental series several recommendations were proposed for the use of the standard U.N. SCB:

- the use of three instead of two band heaters to decrease temperature gradients on the vessel wall;

- the use of an outside thermocouple position between the connection-points of the middle heater;

- using a constant heating rate of 3 K/min by means of a PID control unit. In the case of an extreme energy consumption, caused by a melting material, it could happen that the maximum power of the heaters is not sufficient to maintain a constant heating rate, a constant voltage being then recommended;

- perform the tests with totally confined material to obtain reproducible results.

The heating rate of the SCB can be varied from 1 K/s down to 3.3 K/h.

Scholtes & Makkus (1993) report on a test cylinder type IV being developed at TNO as their ultimate goal is to develop a well instrumented cook-off test for qualification and classification of explosives (see Fig. 2.25).

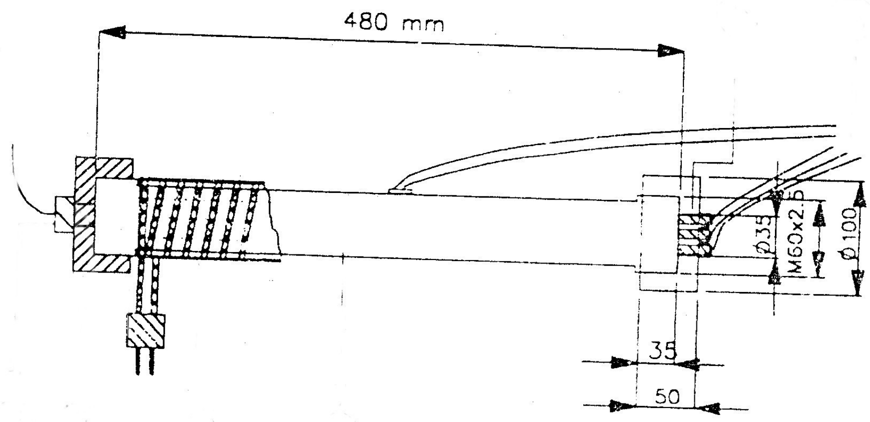

Figure 2.25 - TNO Type IV Cook-Off Test Cylinder.

Scholtes & van der Meer (1994, 1997) report further on improvement on TNO-PML cook-off test and temperature and strain measurements added to the TNO-PML cook-off set up. The strain measurements proved particularly interesting as the results show a trend in the increasing rate of strain of the different phases of the Deflagration-to-Detonation Transition (DDT) experiment. Quantitative analysis was still not possible at this time. The radial temperature distribution curves in the centre of the Cook-Off experiments revealed interesting information about endothermic and exothermic reaction steps, and melting and phase transitions of the explosive substances. The authors state, nevertheless, that following investigations would be more orientated into quantifying the severity of Cook-Off reactions.

Scholtes (1997) reports on current research to improve the TNO Cook-Off Test further. The first pressure measurements were attempted without the expected results. Solutions are presented to the problem. Strain measurements were at this time producing very good reproducible qualitative results, and quantitative statements were expected to be produced coupled with pressure measurements.

Scholtes *et al.* (1997, 1998, 1999a, 1999b, 2001a, 2001b) report on tests performed with the TNO improved Cook-Off tube to assess violence of response and influence of the free volume on the Cook-Off response. The Cook-Off test tube (see Fig. 2.26) comprises a 10 mm thick wall steel cylinder 500 mm in length, with an I.D. of 35 mm and an O.D. of 55 mm. The tube inner volume is 480 cm^3 and is closed at both ends with specially constructed steel end caps sealed with an 'O'-ring. With this cap construction the cylinder can withstand internal pressure up to 240 MPa (quasi-static).

One of the end caps is designed to accommodate for four thermocouples feedthrough assemblies.

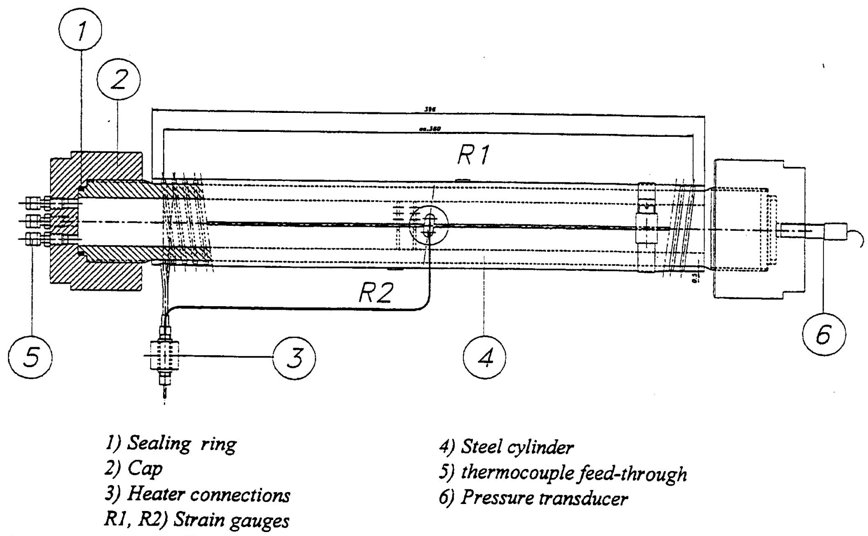

Figure 2.26 - TNO Cook-Off Test Cylinder.

The heating system consists of a long heating wire wrapped around the total length of the tube, and an added heat conducting sealant is placed between the helical loops to improve the distribution of heat flow from the heating wire to the steel cylinder.

The temperature is measured with 6 type K thermocouples: four inside the tube halfway along the cylinder at different positions in the radial direction, the fifth on the outside surface wall of the tube, and the sixth in the outside of the steel cylinder as a control.

A piezo-resistive pressure transducer in the second end cap allows pressures to be measured up to 240 MPa at up to 533 K.

As the actual pressure and the total pressure of the Cook-Off response cannot be measured directly, the indirect methods used at TNO involve amongst others strain measurements techniques. At the present the following strain measurements techniques are being developed:

- Conventional strain gauge: mounted locally in between the heating wire with an operating temperature range up to 643 K. The serious limitation that this technique presents is that only allows measurements in very localised regions of the tube.

- Optical techniques: using an Interferometric system. Two Interferometer techniques have been developed: the Mach-Zehnder and the Sagnac. The extremely complex nature of these techniques has no place in this review.

Several tests on very different explosive and propellant compositions have been tested using this experimental set up and the results are presented on various publications.

Federal Republic of Germany

In the Koenen Test, also known as "*Stahlhulsenverfahren"*, the sensitivity of solid and liquid substances to the effect of intense heat under partial and defined confinement is tested.

The sample is placed, to a depth of 60 mm, in a steel tube (75 mm length and 24 mm internal diameter). A steel orifice plate with an aperture, which can vary in diameter (1 - 24 mm), closes the top of the tube, which is heated by four burners under standard conditions (see Fig. 2.27).

This test is conducted in a protective steel box, as the gases generated by the decomposition of the sample cause a pressure build-up (bursting pressure several hundreds of bars), that may induce fragmentation on the tube depending on the diameter of the orifice plate's aperture. The burners are located at three sides at the bottom of the box, in a position that optimises the tube heating. The number of fragments varies with the diameter of the orifice. By testing the sample with series of apertures, the largest diameter for which the tube is destroyed in at least three fragments is determined – this is designated the *limiting diameter*. The larger this diameter the more violent the energetic material under investigation reacts upon severe heating.

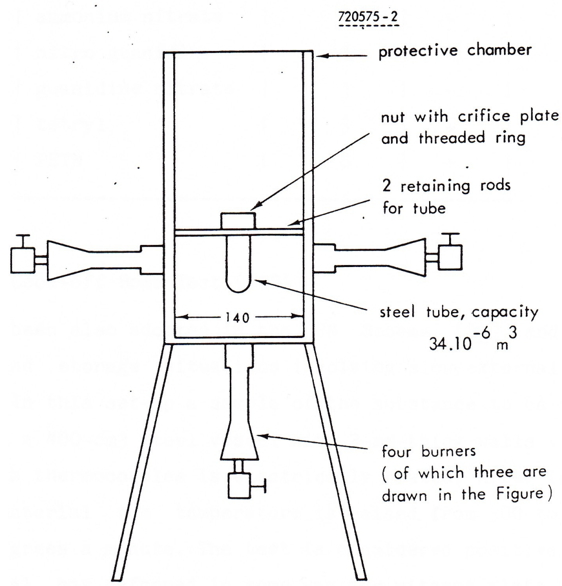

Figure 2.27 - Koenen Test Experimental Set-Up.

This test is mandatory according to the German Law to investigate the safety hazards of energetic materials. The use of this test is now spread and it has been admitted in the U.N. classification scheme. This method presents an advantage by yielding quantitative results in the form of the limiting diameter of the holes in a chrome-steel orifice plate, which covers a steel tube. Some of the results of this test can be seen in the Recommendations on the Transport of Dangerous Goods (1986) (Rooijers & Leeuw, 1987; Boggs & Derr, 1990).

Langer *et al.* (1993) report on fast Cook-Off tests performed at the Fraunhofer-Institut für Chemische Technológie (ICT), using samples in a steel bolt type vessel, 50 mm in diameter and a 100 mm in length, with a 5 mm thick wall. The heating system comprises electrical nozzle heaters at the full length of the cylinder, providing a heating rate of 2 K/s. Temperature measurements are performed by means of a thermocouple. Time to reaction of the explosive and strength of reaction are also assessed, the latter by the fragmentation pattern of the vessel.

Canada

Farinaccio (1991) depicts work on Cook-Off performed at the Defence Research Establishment Valcartier, in a system designed to simulate variable thermal environments with a configuration that best addresses their needs - testing a 155 mm warhead. The methodology used, although following the guidelines of the U.S. DOD-STD-2105 (NAVY) with respect to the heating rate (3.3 K/h), goes a step further by testing three other intermediate heating rates in order to show the influence of the heating rate on the reaction temperature of explosives. To develop these tests it was decided to settle for a representative design of a 155 mm ordnance system with predefined constants of size (5 kg of explosive) and confinement. Thus, a metal cylinder filled with energetic material was subjected to a controlled thermal environment via an enclosed oven (see Fig. 2.28):

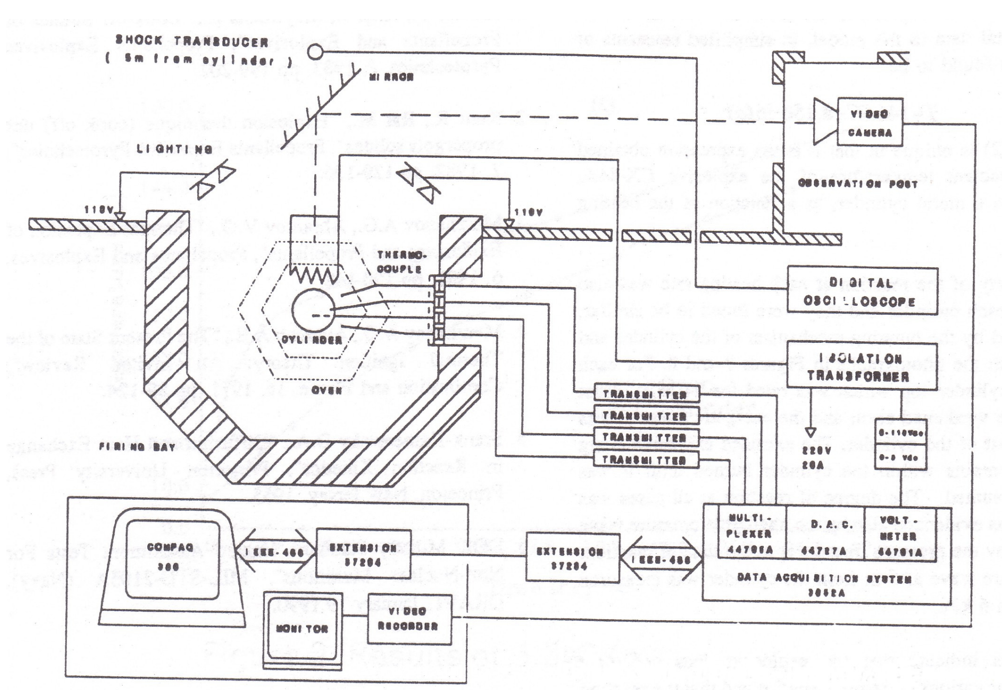

Figure 2.28 - DREV Experimental Set-Up.

The specifications of the design used include a cylinder volume of 3×10^{-3} m^3 and a top cover especially designed to burst at an internal pressure between 22 - 24 MPa, which simulates the munition’s bursting pressure. The heating rates used in this series of Cook-Off tests were 3.3 K/h, 9 K/h, 25 K/h and 75 K/h. The placement of the container within the oven was carefully considered in order to minimise varying heat flux and large air temperature gradients. The heat flow on all surfaces of the container was to depict a free flowing convective and conductive heat transfer. Measurements of time and temperature to cook-off were made.

According to Farinaccio (1991), the Cook-Off method at DREV adds versatility to the existing Cook-Off method described in DOD-STD-2105A by altering the thermal environment of the test sample, as the method attempts to depict thermal environments that simulate tangible hazardous thermal scenarios of munitions of any size and confinement.

Norway

The Norwegian Defence Research Establishment has built a Small Scale Cook-Off Bomb facility, based on the model of Pakulak & Anderson. They classify the level of severity of the explosive reaction by the condition of the witness plates after the event (Scholtes & van der Meer, 1994).

Australia

Stroud (1976) reported on Cook-Off studies being developed in 30 mm DEFA Practice ammunition by means of an instrumented aluminium block isothermally at a 5 K/min heating rate. The specification for this test is in the Explosives Hazard Assessment Manual from the Sensitiveness Collaboration Committee, Manual of Tests, Test No. 3/66, March 1966.

The Materials Research Laboratory at D.S.T.O. has been developing work in Cook-Off since 1980's. Parker (1989) reports the construction of a Super Small Scale Cook-Off Bomb (SSCB), for Fast and Slow Cook-Off tests with samples up 0.02 kg. The explosive sample has the form of cylindrical pellets 15.9 mm diameter and totalling 63.6 mm in length and it is heated at a controlled rate under moderate confinement. The response is assessed by the nature of the damage or fragmentation of the bomb assembly and is usually classed as mild burning, deflagration, explosion or detonation. The fast heating rate is usually 1 - 1.2 K/s and the slow is 0.1 K/s (Dagley *et al.*, 1989a and 1989b; Pisani, 1990; Parker & Dagley, 1996; Dagley *et al.*, 1996). These same authors report, in most cases, good agreement in the Cook-Off results obtained in replicate tests at a given heating rate.

A Small Scale Cook-Off Bomb facility for Fast and Slow Cook-Off tests up to 0.7 kg, based on the Naval Weapons Center (NWC) design (Pakulak & Cragin, 1983 and 1986), has been reported by Jones & Parker (1991). This Cook-Off test has been accepted by the U.N., as a suitable test for classifying energetic materials in regard to their thermal response, as it simulates the hazardous scenarios that can arise from transport, storage and handling.

The reasons supporting the choice for these test facilities are linked with the fact that the use of confined samples and external heating sources results in increased reliability and reproducibility of the results (de Yong & Redman, 1991).

The Australian researchers report on a considerable amount of work on both of these facilities (Parker, 1989; Dagley *et al.*, 1989a and 1989b; Pisani, 1990; Jones & Parker, 1991; de Yong & Redman, 1991; Ho *et al.*, 1993; Ho, 1995; Parker & Dagley, 1996; Dagley *et al.*, 1996) pointing out that these are not free of disadvantages:

- the SSCB is not considered suitable for evaluating the response of materials which melt at temperatures considerably lower than that at which reaction occurs, due to loss of sample;

- the SSCB contains a relatively large void space at the top of the cylinder, and the top confining plate contains a small hole which allows access for the thermocouple. This remains unsealed during the test, thus the gaseous decomposition products are relatively easily vented;

- in the same reported Cook-Off tests the recorded temperature at event was that sensed by a thermocouple in the aluminium liner. The temperature at the surface of the sample at the time of event was then derived from a calibration chart obtained by heating an inert (sand) filled SSCB which had a second thermocouple welded to the inner surface of the inner steel cylinder. There are no direct measurements of temperature at event in the sample;

- the calibration makes no allowance for self-heating prior to reaction. The error due to self-heating in Fast Cook-Off is probably negligible, but in Slow Cook-Off it may be of several degrees Celsius.

Some other problems highlighted by these authors for the case of the SSCB are common to any other tests:

- the Cook-Off results obtained in terms of violence of response differ in some cases from full scale munitions tests. This difference is probably due to the smaller sample mass used in the SSCB test coupled with venting of the combustion products;

- the porosity of the sample, the method of heating and an increase in sample density also appear to strongly influence the severity of the response;

- the reaction violence is determined mainly by the extent of the damage to the vessel. However, it is often difficult to assess the severity of the test response, because the boundaries between the various levels of reaction are not distinct;

- preliminary experimentation with the SCB using an inert explosive replacement and typical heating rates (fast - 1 to 1.2 K/s and slow - 0.1 K/s) showed that the SCB behaviour is not compatible with the assumption of a time independent temperature profile over the end surfaces. Furthermore, heat loss over these surfaces from both radiation and convection was also noted;

- the relative size and placement of the heating bands in the SCB, as these do not cover the entire curved surface of the cylinder, proved experimentally to cause temperature gradients between the side and the top of the vehicle. These experiments verified that the temperature gradient is simply due to the finite time needed for the heat to diffuse from the heating bands to the upper surface of the block;

- these experiments were performed at a very rapid heating rate, and while the radiative and convective heat loss terms are insignificant for this particular regime, this will not necessarily be the case for much lower heating rates used for Slow Cook-Off studies, where the explosive events can take on the order of 20 hours to occur.

Ho *et al.* (1993) reported on work done with propellants in a modified SSCB that allows a more quantitative measure of the reaction violence by means of pressure/energy output measurements. The modification of the SSCB did not alter the test response or the reaction time and temperature, but allowed discrimination between propellants that behave very similarly in the less instrumented test. Extra instrumentation was introduced to assess temperature distribution in some of the propellants during Fast and Slow Cook-Off trials.

The authors went on to define a second criterion of Cook-Off: ease of ignition, which is given by the time-temperature profile obtained during the test. They refer that in contrast to explosives, where the reaction time and temperature are not very different for different compositions (based on the same explosive with different binders), these parameters differ significantly for different classes of propellants with different binder to oxidiser weight ratios. For composite propellants, the oxidiser type dominates this criterion. The results obtained showed that for reaction times the same trends were observed for both heating rates, while for reaction temperature, there is a slight difference for the two heating rates, probably as a result of the non-uniform temperature distribution across the specimen during Fast Cook-Off.

Barrington (1994) reported on full scale Fast Cook-Off (Fuel Fire) tests being conducted on propellants following the STANAG 4240 experimental procedures. A very detailed overview on the background and problems associated with fuel fire testing is depicted by Barrington & Schebella (1994).

Japan

Kimura *et al.* (1997) report Cook-Off work with a test vehicle consisting of a brass pipe (O.D. = 106 mm and I.D. = 102 mm), to simulate a brass case cartridge, steel flanges and four 10 mm diameter steel bolts. A piezo-electric transducer was attached to the vessel through an extension tube to reduce heat transfer in the Cook-Off Test (see Fig. 2. 29).

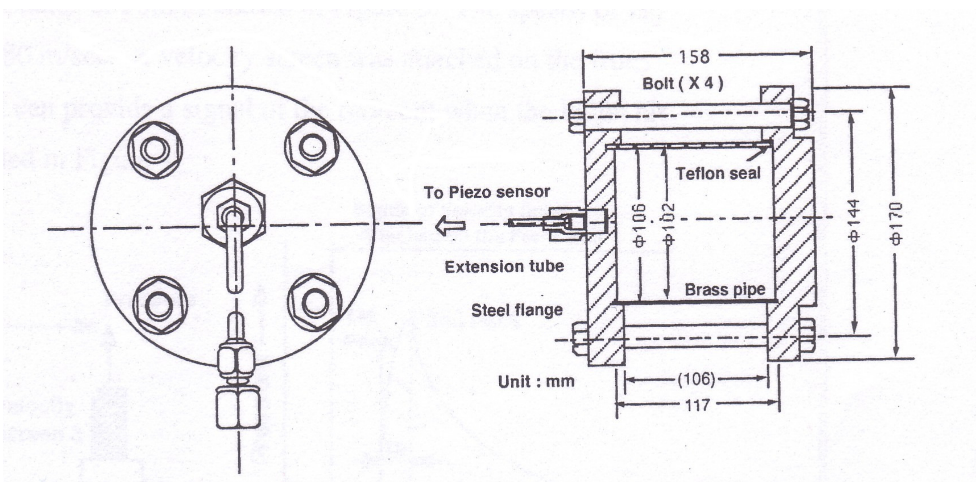

Figure 2.29 - Cook-Off Test Vehicle of the First Research Centre, TRDI, JDA.

The heating system used a propane gas burner (see Fig. 2.30), and the heating rates between 2 K/min and 3 K/min.

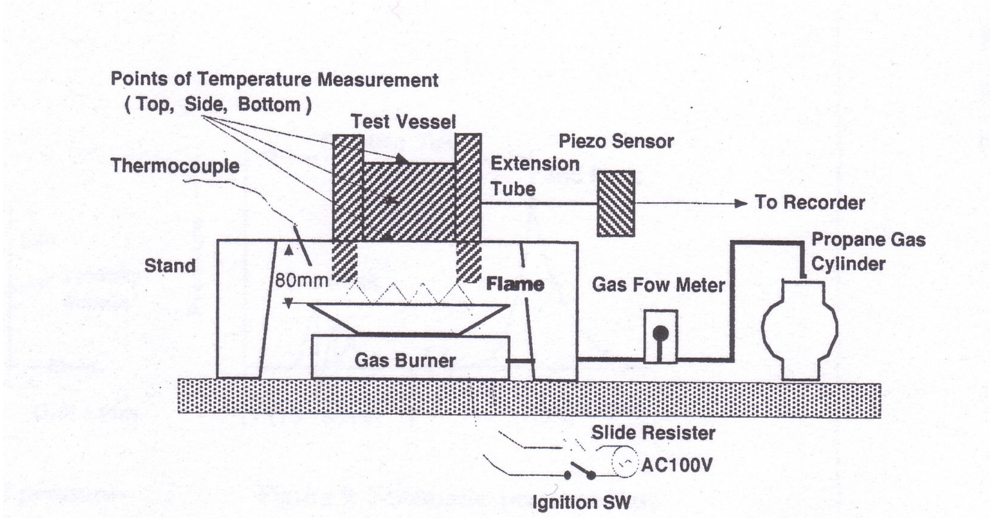

Figure 2.30 - Cook-Off Test Set Up of the First Research Centre, TRDI, JDA.

The waiting time to cause burst of the brass pipe ranged from 7 to 15 min for the propellants under study. The authors observed that for different propellants this time correlated with the temperature of the DSC peak for the material.

Maximum pressures for the test vehicle were approximately 20 MPa. The pressure build up rate in the test vessel was considered as the measure for the severity of the propellants reaction to the thermal stimulus. The rates of pressure in these Cook-Off tests were almost 10 times higher than those obtained in a Closed Bomb Test at a pressure of 20 MPa.

The authors observe that high pre-conditioning temperatures may result in an increase in burning rate.

Comments on the Survey

The above literature review raises several points of discussion:

- Sample Size: small samples, in the order of 2×10^{-3} kg and lower, are not representative of real systems, due to problems mostly of homogeneity and sampling. Furthermore some test vehicles involve the use of several pellets as a sample, thus creating several interfaces that may difficult the use of instrumentation and interfere with the growth and propagation of reaction, therefore inducing changes in the violence of response obtained, and leading to further deviation from the scenarios in real life;

- Sample Storage: some of the tests performed involve storage of the samples between preparation of the samples and actual Cook-Off testing for considerable amounts of time, which can lead to deformation of the samples as referred in some publications;

- Cost of Test Facilities: most of the test facilities described require extremely generous budgets as in most cases they became “violence of response assessment” orientated;

- Cost of Test Vehicles: the high cost of vehicles, particularly if driven by the desire for violence of response assessment makes a statistically significant number of tests unrealistic;

- Existence of thermal gradients in the test vehicles prevents a uniform heating of the test sample, possibly influencing the thermal decomposition mechanisms;

- Estimation of Cook-Off temperatures in explosive samples based on calibration measurements made with inert fillings can lead to very inaccurate Cook-Off data as parameters such as thermal conductivity, thermal diffusivity, chemical mechanisms leading to self-heating and thermal runaway of the explosive system are not being accounted for;

- Non-Intrusive Measuring Techniques: the very core of the problem of using any measuring techniques (thermocouples, pressure gauges, etc.) is summarised in the question “How not to interfere with the system under study and at the same time to gather the most complete set of information about it?”. The measuring instrumentation normally used interferes with the degree of confinement (e.g. drilled holes surface of the container, etc.) and venting, which may lead to less violence of response than what one would expect to observe in a real system, and with mass and energy transfer processes. Furthermore, a harsh thermal environment can cause instrumentation problems due to phase changes, chemical decomposition, thermal expansions, etc.;

- Separate Cook-Off Testing of the Components of a Real System: the separate Cook-Off testing of the multiple components of a real system normally does not lead to a final result that in any way resembles the Cook-Off reaction of the system as a whole;

- Non-Agreement on Nomenclature: the significant lack of consensus on the very basic technical terms referring to Cook-Off creates serious difficulties for the development of any extensive study on this subject;

- Non-Agreement on Slow and Fast Heating Rates Definition: there is no agreement as to what ranges of heating rates are encompassed by the description “fast” and “slow”;

- Non-Standardisation of Testing Methods: creates impossible barriers to the comparison of results, to the agreement on the true meaning of any results, and normally results in duplication of testing by the several nations, institutions and laboratories and all this to large expense.

Taking all these aspects into consideration, and in the view of the available budget for the present study, several decisions were taken into the type of Cook-Off test facility to be established at the Royal Military College of Science/Cranfield University:

- design and construction of a low cost test vehicle with a fixed degree of confinement that would allow time and temperature to Cook-Off to be measured enabling the performance of Cook-Off tests as a fast and reliable method to rank explosives;

- the dimensions of the sample would be no less than a nominal 0.02 kg in order to avoid as much as possible problems related to the homogeneity of the sample and the sample should be formulated and casted (in one single piece) as shortly before testing as possible to avoid extended storage;

- study the possibility of conveniently scaling the test vehicle in stages up to perhaps 2 kg sample size while maintaining the basic simplicity of design and manufacture;

- the test facility should encompass a heating system that would respond reliably to a wide variety of both Fast and Slow Cook-Off heating rates, although the dimensions of the test vehicles to be tested as small and medium scale during this study program already indicate that in spite of widely different heating rates being used it is predictable that these tests will all fall under Slow Cook-Off regimes;

- the assessment of the violence of reaction, due to budget constraints, has to be left outside the scope of this programme. Nevertheless, the testing facility should accommodate for a fragment containment capability in order to allocate further improvements on Cook-Off testing this way allowing for the study of any parameters in future studies.

2.4. MODELLING

Presently, the safety assessment of energetic material or munitions systems involves extremely high costs for the limited information that it in reality provides. The data gathered is, in most cases, difficult to interpret and does not allow normally for extrapolation to other systems or generalised conclusions.

If in one hand, there is the problem of the too costly full-scale trials that lead to non-statistical information and limited data specific to limited thermal environments; on the other hand, there is the problem of the small scale testing, as it brings a lot of instrumentation into a scenario that one would wish as close to reality as possible. Furthermore, in the case of designing and developing new energetic materials or ammunitions systems the data gathered by small scale testing can present difficulties in scaling up.

Therefore, modelling presents itself as a very cost-effective tool as it allows a very high number of calculations, considering a very much wider range of thermal environments, with a single model, accommodating simultaneously for thermal scenarios that cannot be experimentally tested, at relatively low cost.

Modelling can also provide insight for both mechanisms and effects. Furthermore, when combined with design process calculations it can be used simultaneously to aid the design of munitions with reduced Cook-Off vulnerability, avoid the need for expensive retrofits and aid their safety assessment (Belcher *et al.*, 1991; Fleming, 1995; TEEMAC, 1998).

There are several works published on modelling concerning safety assessment of munitions on their response to thermal unplanned stimulus. Zinn & Mader (1960) and Zinn & Rogers (1962) were the first to calculate temperature profiles and times-to-explosion by numerical methods, which were in good agreement with experimental results. From then onwards many have used numerical models to describe cook-off phenomena with success (Boggs & Derr, 1990).

The finite difference method (Richtmeyer & Morton, 1967) is the most widely used. In the U.S. finite difference methods have been used to model the times-to-explosion of several high explosives simulating numerically the ODTX (Boggs & Derr, 1990; Dagley *et al.*, 1996).

Numerical methods have been applied in France to investigate and understand the thermal decomposition of propellants, based on the Zinn & Rogers model, having reached a satisfactory agreement between theory and experiment. Likewise in the Netherlands, numerical methods have been used for the decomposition of unstable compounds in electroexplosive devices (Boggs & Derr, 1990).

Jones & Parker (1991) report on some preliminary heat flow calculations for the MRL/DSTO SCB test apparatus, performed with the HEAT computer code to ascertain the suitability of the code for modelling the thermal environment in the SCB test. The HEAT code is a reactive multi-material finite difference FORTRAN computer code for the solution of the diffusion equation in two dimensional axisymmetric cylindrical geometry. According to the authors, it allows for a maximum of three separate nested materials, and in a typical application the innermost material will be an explosive. This code allows, therefore, the innermost material to undergo a phase change and also to decompose via zero order Arrhenius kinetics. Numeric simulations were performed to predict temperature-time profiles at specific positions within an inert filled SCB. These predictions were compared with temperatures obtained from thermocouple measurements made on the SCB apparatus, and showed good general agreement and justified the continued application of HEAT to the SCB. However, recommendations of modifications to HEAT are made in order to increase the accuracy of the calculations.

Ho (1995) states that although the Cook-Off initiation temperatures and times can be readily modelled/predicted by heat transfer analysis, there is currently no simple method to predict the reaction violence, as many of the essential energetic material, case and dynamic confinement parameters are not known or can't be reasonably estimated. The development of satisfactory prediction methodologies and modelling tools for Cook-Off reaction violence requires the physico-mechanical and thermal properties of the energetic material, case (e.g. yield strength), etc., to be known as a function of temperature, pressure and heating rate.

The same author gives the example of the geometry of the energetic material in the ordnance item is dependent on the phase/state changes with the temperature. A previous study on the Cook-Off behaviour of rocket propellants is mentioned as it showed that thermomechanical properties have some influence on the thermal distribution within the test specimen, because of the change in heat transfer characteristics with viscosity and/or modulus of the energetic material (soft polymeric materials generally have a lower thermal conductivity and higher specific heat and therefore lower thermal diffusivity than hard polymeric materials).

Ho (1995) refers also that there have been numerous studies on the characterisation of the Fast and Slow Cook-Off behaviour of energetic materials, but little detailed information is available on the pressure and temperature dependence of the physico-mechanical and chemical kinetic parameters of the energetic material and their relation to Cook-Off behaviour.

Dagley *et al.* (1996) addressed the effects on the thermal response of pressed polymers bonded explosives caused by varying their components assessed at two extreme heating rates. The systems studied consisted of RDX-based compositions containing 5% ethylene-vinyl acetate binder with varying amounts of PETN and TATB. Some of the experiments were numerically simulated using a one-dimensional finite difference code. The simulations were not able to predict the violence of thermal response, but do accurately reproduce radial heat flow in the test assembly and satisfactorily predict both the time to thermal response and the surface temperature at the response for the mixed explosive compositions at both fast and slow heating rates. The calculations clearly demonstrate the need to include the temperature dependence of the material properties of the material and a kinetic decomposition scheme appropriate to the degree of confinement, before good agreement between simulate and experimental results for surface temperature at response time and time to response can be obtained.

The authors mention that a more detailed understanding of the fundamental mechanisms involved in the progress of burning through deflagration to detonation under Cook-Off conditions is required before numerical simulations to predict the nature of the response can be attempted.

Fleming (1995) refers work done in AWE (U.K.) using models involving a customised version (X-TRUMP) of the finite difference code TRUMP and experiments made on an ODTX apparatus in order to validate the model. It was adopted a scheme based on the best available mechanistic information and kinetic data and thermodynamic data for the reactants and thermally important intermediates and normalised the model to high quality time-to-explosion data.

When attempting to validate the model used, Fleming refers that the calculated times and surface temperatures were in excellent agreement with the measurements made when medium scale experiments were carried out on a cylindrical assembly containing a TATB/HMX-based main charge explosive, an HMX based booster and an exploding bridgewire detonator. Nevertheless, the same author refers that on Slow Cook-Off experiments of a depth charge the agreement of the time-to-explosion with the trial data was disappointing although the case temperature of the explosion was reasonably close. When trying to perform calculations with this data using a first order decomposition scheme the results proved to be wildly optimistic, therefore pointing for the necessity for better data on the chemical and physical properties of explosives components.

Taking this work further an attempt was made in AWE (U.K.) to try and model the magnitude of explosive response. The magnitude of response depends on the weapon design and the thermal environment to which it is exposed. Some qualitative judgements can be made through inspection of data from reactive heat flow calculations and of the anvils used in experiments, but further work needs to be done to develop a quantitative predictive capability (Fleming, 1995).

Belcher *et al.* (1991) studied a variety of plastic bonded explosives under confinement at various constant elevated temperatures in a laboratory apparatus in order to determine the time-to-explosion. The experimental data collected on HMX, HMX/NC, TATB, TATB/HMX, RDX/HMX and PETN containing explosives were successfully modelled using a reactive heat flow code, which contained chemical decomposition kinetics descriptions composed of several reaction steps and reacting species.

Furthermore, numerical simulations of larger scale experiments and more complex configurations of main charges explosives and initiation trains accurately predicted the influence of time to ignition of changed scale and geometry and provided valuable insights into the factors governing the magnitude of explosive response.

These calculations were performed using a version of the general purpose finite element difference heat flow code TRUMP customised by the present authors to accept multi-step, multi-species reaction schemes of arbitrary complexity.

Chidester *et al.* (1997) have been engaged on the development of computer models to describe the entire explosion process in terms of heat flow into the explosive, chemical decomposition of the explosive, time and location of the resulting thermal runaway, subsequent deflagration of the remaining heated explosive and the interaction of the reaction product gases with the confining materials. The work done involves calculations made with the CHEMICAL TOPAZ code. This code is a multi-step chemical kinetic and multi-material version of the finite element heat transfer code TOPAZ2D. Chemical TOPAZ reproduces the previous results obtained using the TACO2D, but constitutes a more general treatment of both the chemical kinetics and the mixture of the explosive and its decomposition products.

The main advantage presented by this code lays on the fact that it allows one to describe the reacting explosive and its intermediate and final products as a mixture in which each component has its own thermal conductivity and heat capacity dependencies on temperature. Previous calculations using the TACO2D were based on assumed average thermal conductivity and heat capacity versus temperature curves for the entire mixture. Furthermore, TACO2D was also limited to three or four species and a similar number of reactions and did not include pressure dependent effects. Chemical TOPAZ mixture can contain any number of components and any number of chemical reactions with specified frequency factors, activation energies, and heats and orders of reaction.

Chemical TOPAZ also allows ideal gas pressures calculations based on the concentrations of gaseous species present for use in pressure dependent reaction rates and to estimate the total pressure produced by the decomposition. A maximum value of the total pressure is used to simulate the burst pressure of the confinement.

Chidester *et al.* (1997) concluded that the heat transfer into the explosive and the time and location of the resulting thermal explosion were accurately calculated by the Chemical TOPAZ code. The subsequent work of gaseous reaction products on the confining metal cylinder was accurately calculated using a two-dimensional pressure dependent deflagration reactive flow model. Furthermore, thermal, chemical kinetic and reactive flow hydrodynamic modelling of the violence of these thermal explosions yielded quite accurate simulations of this type of event.

The authors alert, nevertheless, for the fact that a great deal more of experimental work, metal fragmentation models, and the development of 3D coupled thermal-chemical-mechanical computer codes are required before completely predictive tools are available to assess the violence of thermal explosions and the subsequent effects on their surroundings.

McIntosh (1996) published an extensive report on work performed at DREV, Canada, on 57 mm warhead Cook-Off simulations using TOPZ2D. This study will not be reviewed here.

Hobbs, Baer & Gross (1994b) state that Cook-Off modelling of confined materials involves the coupling of thermal, chemical and mechanical effects, while in the past modelling had focused only on the prediction of thermal runaway with little regard to the effects of mechanical behaviour of the energetic material. To address the mechanical response of the energetic material, a constitutive sub-model has been developed by these authors, which can be incorporated into thermal-chemical-mechanical analysis. The authors present in this work the development of the above mentioned sub-model and its incorporation into a fully couple one-dimensional, thermal-chemical-mechanical computer code to simulate thermal initiation of energetic materials. Model predictions include temperature, chemical species, stress, strain, solid/gas density, yield function, and gas volume fraction. The sample studied is a sealed aluminium tube filled with RDX exposed to a constant temperature bath at 500 K.

This micromechanical sub model is based on bubble mechanics, which describe nucleation, decomposition, and elastic/plastic mechanical behaviour. As such this constitutive material description requires the input of temperature and reacted fractions of energetic material as provided by the reactive heat flow code, XCHEM, and the mechanical response is predicted using a quasi-static mechanics code, SANTOS. A parametric sensitivity analysis indicates that a small degree of decomposition causes significant pressurization of the energetic material, which implies that Cook-Off modelling must consider a strong interaction between thermal-chemistry and mechanics.

Hobbs, Baer & Gross (1994c) report on a Thermally Reactive, Elasto-plastic eXplosive code (TREX), which has been developed to analyse coupled thermal, chemical and mechanical effects associated with Cook-Off simulation of confined or unconfined energetic materials. According to these authors the reasons behind the development of this code are related to recent experimental work that a small degree of decomposition has a profound influence on pressure build up and/or material expansion. TREX is a one dimensional code composed of three modules, which consist of a thermal/chemistry solver, XCHEM, a static mechanics code, SANTOS, and the constitutive material model, REP. TREX uses an operator splitting technique in which the thermal/chemical fields are advanced using a fixed mechanics field. The mechanics are then advanced over the same time interval using the updated thermal/chemical. This technique provides for a rapid solution since the mechanical solver is inactive during the small time steps required by the thermal/chemistry solver. The thermal chemistry solver is an adaptive gridding method-of-lines code and the mechanics solver is a finite element code with a fixed number of elements. Mesh interpolation is required to communicate the temperature and reacted fraction from the thermal chemistry code to the quasi-static mechanics code. The REP constitutive model is incorporated as a material module for SANTOS to determine stress history associated with a given strain history. Strain is passed back to XCHEM in the form of an expanded or contracted grid. Gaps may form between layers of materials which are used to determine thermal contact resistance between layers. Stress is communicated from SANTOS to XCHEM as mixture pressure which may ultimately couple to pressure dependent combustion mechanisms. Predicted spatial history variables include temperature, chemical species, principle stress, engineering strain, solid/gas pressure, solid/gas density, local yield stress, and gas volume fraction. The gas volume fraction can be used to calculate the specific surface area if the initial nucleation density and physical sizes of defects of energetic materials are known or can be estimated. Confined ODTX experiments were simulated using TREX as pressure failure at 1500 atm. The spherically confined ODTX simulations compared favourably to experimental data for TATB and PBX9404.

Baer *et al.* (1994) describe multidimensional thermal/chemical modelling as an essential step in the development of a predictive capability for Cook-Off of energetic materials in systems subjected to abnormal thermal environments. These authors present work performed with COYOTE II, which is a state-of-the-art two- and three-dimensional finite element code for the solution of heat conduction problems including surface-to-surface thermal radiation heat transfer and decomposition chemistry. Multistep finite rate chemistry is incorporated in COYOTE II using an operator splitting methodology: rate equations are solved element-by-element with a modifier matrix-free stiff solver, CHEMEQ. COYOTE II is purposely designed with a user-orientated input structure compatible with the database, the pre-processing mesh generation, and the post-processing tools for data visualization shared with other engineering analysis codes available at Sandia National Laboratories. Mechanical effects were not at this stage considered in COYOTE II, but the formalism for including mechanics in multidimensions was under development.

The authors emphasize a numbers of features that make COYOTE II a unique tool: a conjugate gradient iterative solver capable of solving problems with a large number of elements, dynamic time stepping, the hemicube view factor routines capable of solving problems with a large number of surfaces, a stiff solver applied to the chemistry equations, and the availability of a large number of user friendly pre- and post-processing support software.

In this study several Cook-Off calculations in order to demonstrate the code capabilities are presented:

- a reactive heat transfer is solved simulating a proposed NAWC benchmark Cook-Off experiments, in which a partially filled container of propellant is heated in an oven. In this case, model predictions for varied heating conditions indicate that the location of ignition occurs at an interior location during slow heating and at a higher heating condition nearer the heated boundaries;

- as a demonstration of reactive heat transfer in a complex three-dimensional geometry, the thermal field in a rocket motor, a star-grained propellant in a rubber-lined stainless steel casing, is modelled using boundary conditions typifying a fire source.

Further studies related to multidimensional adaptive meshing methods for finite elements are presented (such as the calculation of the heat transfer in a component containing an energetic material, subjected to a moving heat source) as an assessment of adaptive meshing strategies to be implemented in COYOTE II.

Maienchein & Nichols (1997) report on development of analytical tools for the Ignition and Initiation Phenomena Program focused on the prediction of the violence of Cook-Off response for energetic materials and their systems. They are developing the ALE3D computer code and measuring key response parameters for HMX-based energetic materials for application in ALE3D.

ALE3D is according to these authors a fully coupled thermal/chemical/mechanical hydrocode that can incorporate all such processes during the relatively slow heating of the energetic material and also during the rapid ensuing reaction wherein the degree of violence is determined. In this study it is described the status and the developing plans for the code and modelling results are presented for the US Navy Variable Confinement Cook-Off Test, which has been identified as a test case for development of predictive capability. The key parameter under study is the burning rate at high pressures and temperatures characteristic, 10 - 600 MPa and 300 - 453 K respectively, of Cook-Off environments and the explosive system is LX-04.

These authors state that ALE3D offers arbitrary Lagrangian-Eulerian treatment of problems for optimum analysis and includes fully coupled thermal transport and generalized, fully coupled chemical reactions. A capability for implicit and explicit timestepping, with automatic switching from one to the other has been incorporated into the code. This allows the calculation of very slow thermal events and very fast hydrodynamic events, just as occurs in Cook-Off, in one code.

One of the main advantages of the code is that it offers the potential to treat the entire Cook-Off issue, including hydrodynamic violence of reaction, in one calculation: Cook-Off response inherently involves chemical reaction kinetics, thermal transport, and mechanical response. During heating, a typical energetic material will expand (perhaps with increasing porosity), lose physical strength, and begin to undergo chemical decomposition. In addition, the external container is also being heated, with loss of physical strength. ALE3D offers the ability to integrate all of these aspects because each aspect may control the overall reaction under different conditions.

In order to apply ALE3D to thermal response problems the authors mention several improvements made to the code: inclusion of heat flow, chemical reactions driven by heat, the formation of mixtures from the chemical reactions, the resultant properties of the mixtures (thermal, mechanical, and equation of state), and the overall response. Thermal mechanisms include thermal diffusion, phase change, thermal contact resistance, and boundary conditions defined in terms of flux, temperature, thermal radiation, and convection. In addition a proportional, integral, derivative (PID) controller is modelled in ALE3D for the evaluation of experimental data taken with such controller. The authors refer also that a bounded temperature boundary condition may be used in which the boundary temperature sets the minimum temperature at that point; however, exothermic reactions can drive the temperature higher than the boundary condition. As for mechanical mechanisms these include volumetric adiabatic expansion, elastic-plastic work heating, sliding friction, gravity, and boundary conditions defined by velocity, pressure, or rigid surfaces. Unlimited chemical reactions may be included, and detonation may be modelled as a chemical or mechanical occurrence.

Other improvements to the code include treatment of virtual slide surface elements, zonal heat generation for elements containing mixtures, thermal subcycling to improve temperature convergence, species advection within elements and during implicit calculations, implementation of reversible and irreversible stress-strain work heating and an analytical mixture model to include solid thermal expansion. Currently, mixtures of gases and solids are modelled using a simple gamma-law gas formalism and an elastic solid with thermal expansion, allowing analytical solution of the mixture equations. Implicit and explicit timestepping capability has been refined as well.

Knock (2000) reports on a one-dimensional Cook-Off code being developed at the Royal Military College of Science/Cranfield University to be able to measure Cook-Off times and parameters for new explosive compositions and that would be able to automatically calculate the kinetic parameters of the explosive by input of the Cook-Off data. The author mentions that this code can work in spherical or cylindrical co-ordinates to model the Cook-Off of an explosive and can deal with two cases: Slow Cook-Off when the boundary temperature is raised slowly over time and Fast Cook-Off when the sphere is placed inside aluminium anvils that have been preheated to a predetermined temperature (e.g. ODTX). The code also includes an optimiser that automatically alters the parameter values to give the best fit to the experimental data. The data input is based on ODTX experiments. The numerical model includes: multi-equation chemical models, pressure burst or all burnt burst, varying or constant boundary temperature, melting of explosive, temperature dependence of physical parameters, automatic optimisation of parameters – physical and kinetic.

Further work published on TREX, TREX3D, COYOTE, and ALE3D can be found in the publications by Hobbs *et al.* (1994a, 1994b, 1995), Hobbs & Baer (1995), Baer *et al.* (1995a, 1995b, 1996, 1998), Schmitt & Baer (1997), Sandusky *et al.* (1998), Atwood *et al.* (1999) and Ho (2000) as only a brief review of the modelling was intended here, which cannot comprise the full extent of the complexity of such codes.

Theoretical simulation based on numerical methods seems a very powerful way for getting an idea for the behaviour of energetic materials and ammunition systems when submitted to thermal stimuli. Nevertheless, the need for a fast development of models and their validation is still very significant.

One of the strong consensus that arose from the TEEMAC Open Workshop on the Influence of Modelling on Terminal Effects and Energetic Materials Research (1998) is the belief that testing and calibration of existing models against experimental data is needed, as well as the need to continue the trend of developing more scientific based models and abandon as much as possible the empirical global descriptions.

Chapter III

EXPERIMENTAL WORK

3.1. TEST FACILITY

The Cook-Off test facility was established in an existing licensed test cell, which required minimum refurbishment and weatherproofing to bring it up to the mandatory standards.

For both Fast and Slow Cook-Off programmes, and at small and medium scales, the test vehicle was positioned inside a fragment containment box designed to allow adequate venting of blast, while easing collection of the fragments of the trials' vehicle. The fragment containment box was placed at the end of the firing chamber (Fig. 3.1).

Figure 3.1 - Firing Chamber Showing Fragment Containment Box.

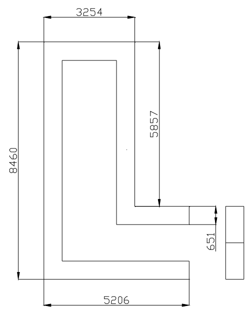

Figure 3.2 - Plan of the Firing Chamber (mm).

The controls for all the sensors and measuring equipment (temperature controller, data acquisition system for thermocouples, CCTV system with IR capability and video recorder) were placed in the control room separated by protective walls from the firing chamber. All operations were conducted remotely (Fig. 3.3).

Figure 3.3 - Control Room.

The cylindrical stainless steel Cook-Off test vehicle with a sample was wrapped in a glass fibre insulated Nichrome heating wire and subjected to a Fast or Slow Cook-Off profile.

A Coulton Instruments Temperature PZX4 Controller controlled the heating of the vehicle.

Two K-type thermocouples are positioned on the inside of the test vehicle in order to record the temperature of the wall and the centre of the charge. The heating rate was controlled by the thermocouple at the wall, which was simultaneously connected to the temperature controller and the data acquisition system. The temperature controller allowed up to four programme options.

Furthermore, an extra K-type thermocouple was placed on the external surface of the test vehicle (clamped between the surface and the wrapped insulated heating wire) to monitor the heating wire temperatures and another one was clamped on the external surface of the containment box, in order to provide an insight on the containment box temperature at the time of an event.

A Grant Squirrel 1005 data logger was used to record all these temperature readings during the entire duration of a trial.

For the trials the test vehicle, filled with the energetic material to be tested and completely wrapped in an insulating material, was placed inside the containment box and the box closed.

In case of an event, all the heating, control and data acquisition systems were brought to a halt and the data transferred into a PC. If the temperature reached the maximum stipulated 673 K, and no explosive event had occurred, then the heating system was switched off and the test vehicle temperature allowed to fall to ambient temperature.

3.1.1. Bunker

The test cell was built of concrete blocks 0.6 m thick considered adequate to contain the most violent possible explosive response of the test sample. This assessment was performed by means of calculations with a software code BLASTX - Explosions Inside Multiple Room Structures, which is widely used for such purposes (see Appendix II).

3.1.2. Fragment Containment Box

The fragment containment box was a bolt type solid steel box, of external dimensions 550 mm x 550 mm x 550 mm, reinforced by weld on all the joints of the 25 mm thick steel plates. In the top of the box there was a permanent opening of 124 mm internal diameter.

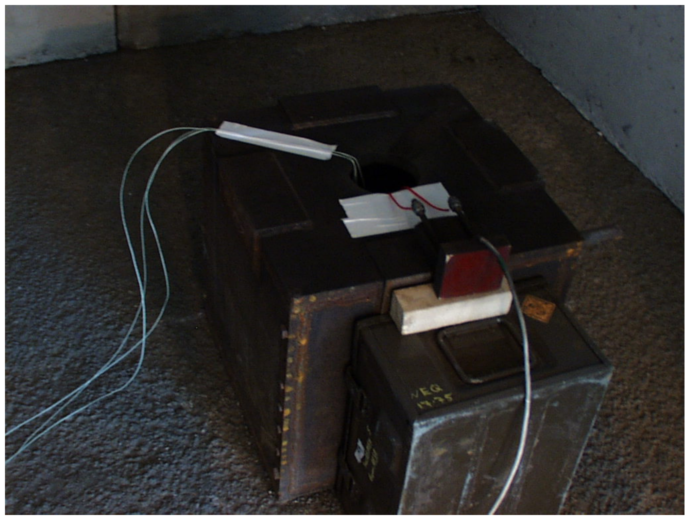

Figure 3.4 - Fragmentation Containment Box.

Calculations were performed on a software code BLASTX - Explosions Inside Multiple Room Structures, CONWEP and PSADS - SpAnw in order to confirm the suitability of the fragment containment box to survive the violence of response of the firing program pre-established (see Appendix II).

The ability of the box to survive the firing program proposed was confirmed by these calculations.

3.1.3. Temperature Controller Box

The Electrical Workshops - Technical Support Services, at the Royal Military College of Science/Cranfield University, were requested to provide for a box to contain the Coulton Instruments Temperature PZX4 Controller. This box comprised a power supply unit, a solid relay unit and the PZX4 temperature controller element.

The power supply unit comprises several integrated circuits that were designed and cut into a FR4 Single Sided Copper Board (e.g. sandwich of copper plates and glass fibre) by an LPKF Proto Mat 91 S CAD system: a transformer, a bridge rectifier, an electrolytic capacitor and a Tantalum capacitor of 1µV.

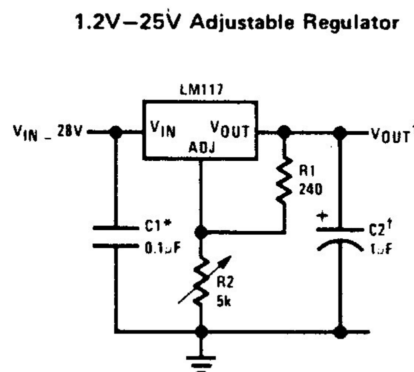

Figure 3.5 - Circuit of the Adjustable Power Regulator included in Power Supply Unit for the Temperature Controller Box.

In this circuit presented above, R2 is a Variable Resistor, R1 the main Resistor, and C2 a Tantalum Capacitor.

This single sided copper board was then treated in a Seno Tin Powder solution at ambient temperature. This treatment lasted for an hour in order to get a 5 µm thickness of deposition. After final treatment of the board, the several components (temperature controller, power supply unit, solid relay unit) were then placed and connected in the box according to the various manufacturers' instructions.

3.2. DESIGN & CONSTRUCTION OF A SMALL SCALE COOK-OFF TEST VEHICLE

The small scale test vehicle was a modification and improvement of an existing piece of hardware of approximately 0.012 kg RDX/TNT capacity. This was scaled up to a nominal capacity of 0.2 kg for the medium scale test vehicle, with the aim of providing basic experimentation for the manufacture, outside this project, of a large scale vehicle of 2 kg capacity.

With the emphasis on low cost, both vehicles were manufactured from the widely available EN3 low carbon steel.

3.2.1. Existing Small Scale Test Vehicle

The vehicle was cylindrical for ease of manufacture, and with uniform cross section likely to allow a uniform temperature distribution, and for future simplicity of modelling. It had a bolt-type configuration, which although not the most modern type of Cook-Off testing devices is the most widely used configuration, based on a design by Cartwright (R.M.C.S.), which had an internal diameter of 20 mm, an internal height of 35.4 mm and a wall thickness of 3 mm. The bolts used were 5 mm. The end caps were 5 mm thick with a 5 mm thick and 22 mm deep flange (see Fig. 3.6 & 3.7).

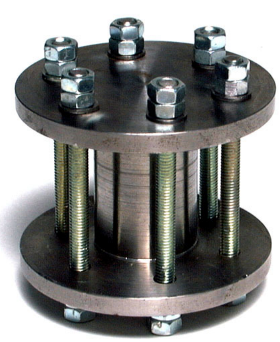

Figure 3.6 - Existent Experimental Cook-Off Test Vehicle.

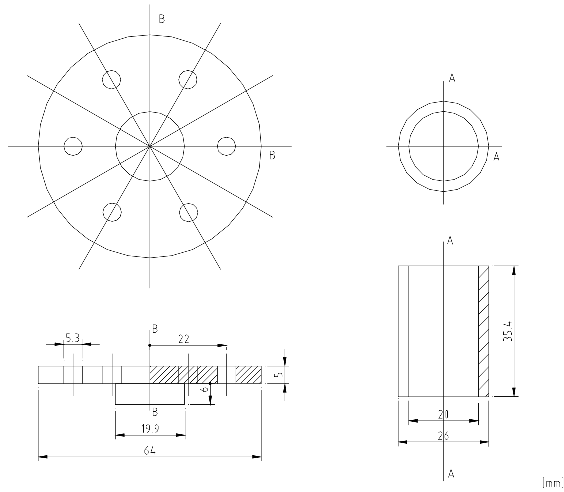

Figure 3.7 - Existent Experimental Cook-Off Test Vehicle.

Thin copper washers were used to seal the caps against the body of the vehicle. The following preliminary tests were carried out to evaluate the design:

- Mechanical Stress;
- Temperature Gradients;
- Mechanical Integrity.

3.2.2. Mechanical Stress Failure Tests

The failure pressure of the test vehicle was obtained by measuring the mechanical stress failure of the bolts using a Houndsfield tensometer, which would however accommodate only the small scale bolts, and an Instron tensometer, which would take both sizes.

Several configurations of nuts on each end of the bolt were tested: 1 nut on each end, 1 + 2 nuts and 2 nuts on each end. Each bolt had an external diameter of 4.86 mm. The cross sectional area (C.S.A.) of bolt used in these tests was of 18.54 mm^2.

The results are given in Figures 3.8, 3.9 and 3.10.

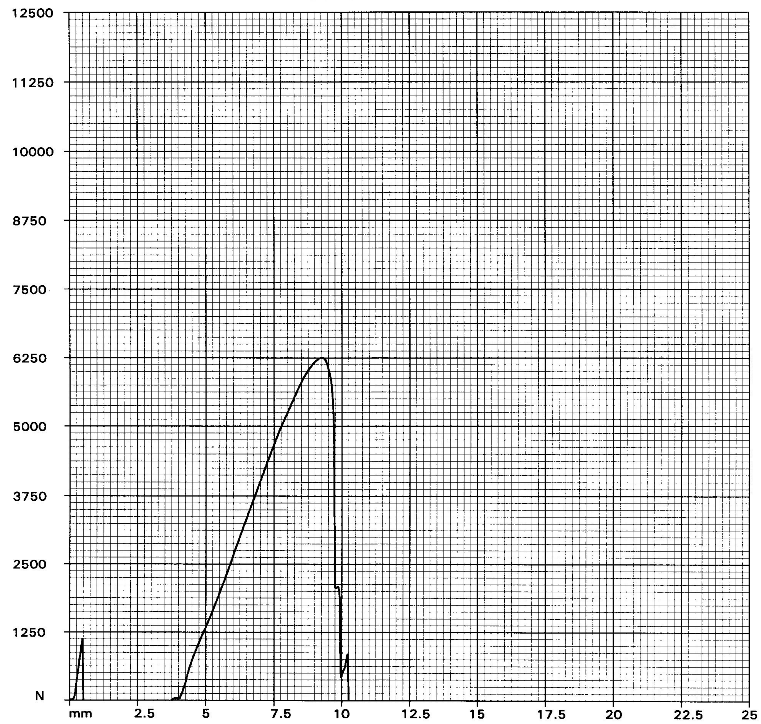

Figure 3.8 - Failure Stress (N) vs. Elongation (mm) - Configuration 1+1.

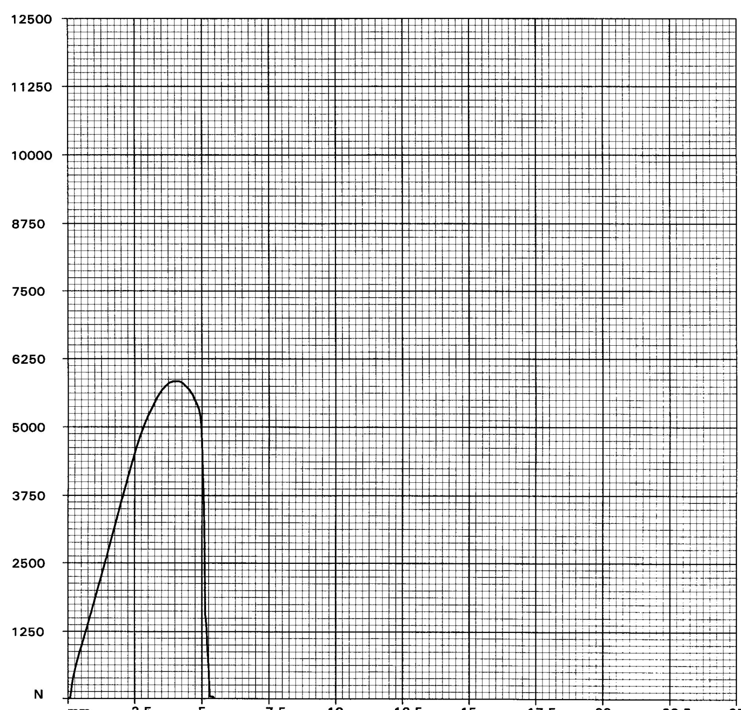

Figure 3.9 - Failure Stress (N) vs. Elongation (mm) - Configuration 1 + 2.

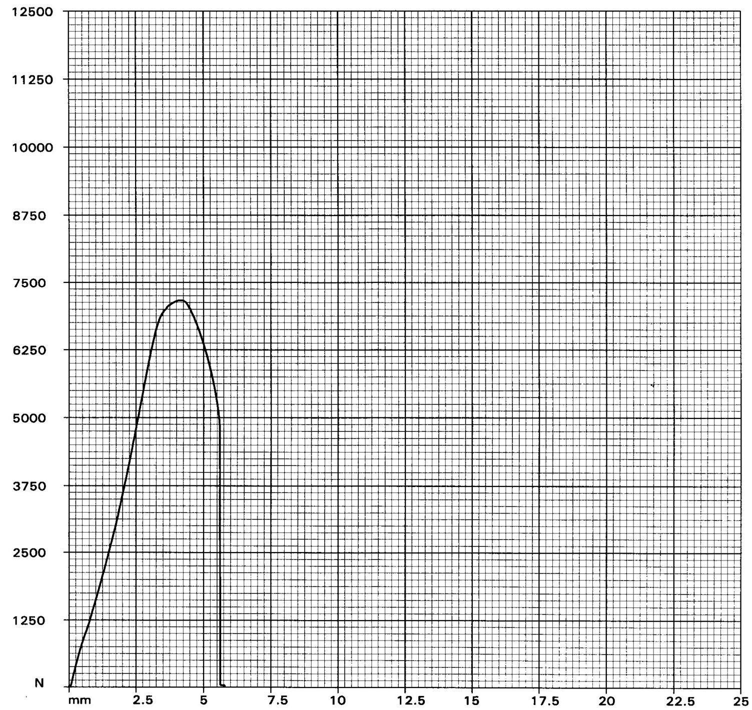

Figure 3.10 - Failure Stress (N) vs. Elongation (mm) - Configuration 2 + 2.

Table 3.I summarises the values obtained for each configuration tested.

Sample	Failure Stress/Bolt (± 5 MPa)
1 + 1	338
1 + 2	315
2 + 2	387

Table 3.I - Stress Failure Limits for Tested Samples.

Double nuts at both ends of the bolt ensured that failures occurred on the shank of the bolt and not at the nut threads. Sister bolts were tensile tested and failed at 386.8 ± 5 MPa. Therefore, with six such bolts the highest operation pressure of the vehicle structure is 2321 MPa before failure of all six bolts. Changing the tensile strength of the bolts can vary this. Considering the vehicle structure has an UTS of approximately 390 MPa and that the material used is an EN3 mild steel (Ys = 250 MPa), the vehicle structure will yield at 1450 MPa (Mustey, 2000; Doig, 2001).

3.2.3. Assessment of the Temperature Zones of the Test Vehicle

Preliminary tests were performed in order to assess thermal gradients in the test vehicle: wall temperature distribution, internal chamber temperature, top end cap temperature and internal chamber temperature radial distribution.

Wall Temperature Distribution

The wall temperature distribution was measured with three K-type thermocouples placed at various locations around the outer surface of the cylinder sample container, while the vehicle was heated with a Eurotherm Mark 1 heating cord system attached to the outer surface of the test vehicle wall, which provided variable heating rates and temperatures when connected to a 220 V variable voltage Variac. The thermocouples were positioned one close to each end cap (thermocouples TC 1 and TC 2) and the one at the centre of the chamber body (thermocouple TC 3). These were used to assess the existence of different temperature zones on the wall (see Fig. 3.11).

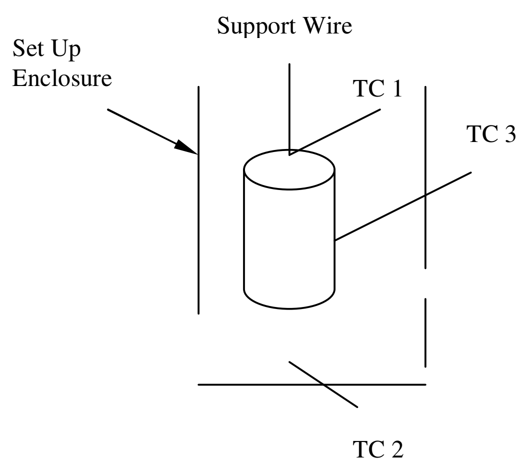

Figure 3.11 - Experimental Set Up Used for Determination of Wall Temperature Distribution.

A 1200 Series (12-Bit) Squirrel Meter/Logger was used to record the measurements. Results obtained during a 6000 s test, with readings being taken every 600 s, are illustrated on Figure 3.12.

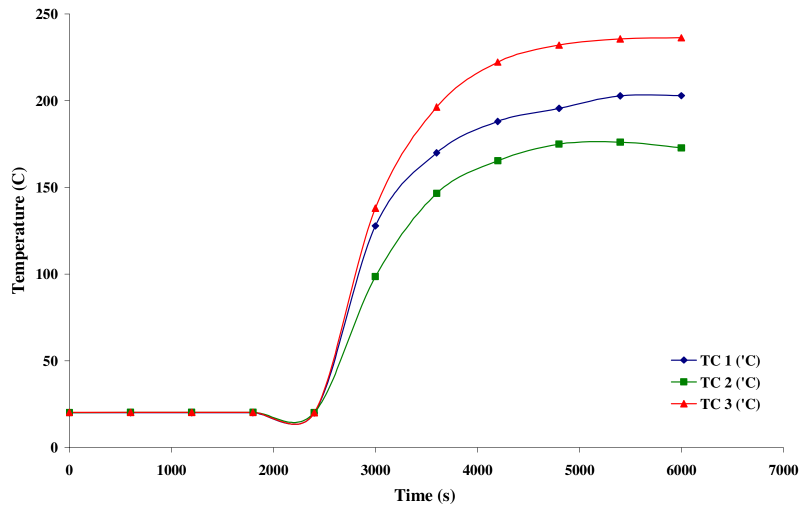

Figure 3.12 - Temperature Zones on the Test Vehicle.

From the obtained results it is possible to observe that (see Fig. 3.12):

- there are some temperature gradients between the different surfaces that could be due to the thickness of the insulation of the heating wire overlapping between wraps of the test vehicle;

- retention of the mechanical integrity of the thermocouples' locations during the experiments is of paramount importance. Movement of the sensors' heads during the heating test at elevated temperatures produced inaccurate values.

Measures were taken to eliminate the movement of the sensors, by replacement of the heating wire with a hot-air heating system. The latter constitutes a safe and simple heating system that allows for easy attainment of temperature and constant heating rates and, simultaneously, for an easier location of the thermocouples and constancy of position, hence eliminating the apparent temperature gradient across the test vehicle.

Internal Chamber Temperature

A test was performed in order to evaluate the internal wall temperature of the test vehicle. The experimental set-up used for this test comprised (see Fig. 3.13):

- a hot-air heating system;

- an empty test vehicle with a top end cap, where a 1 mm diameter orifice was drilled on its centre;

- a K-type thermocouple placed at the centre, at half height, of the empty test vehicle chamber;

- a 1200 Series (12-Bit) Squirrel Meter/Logger.

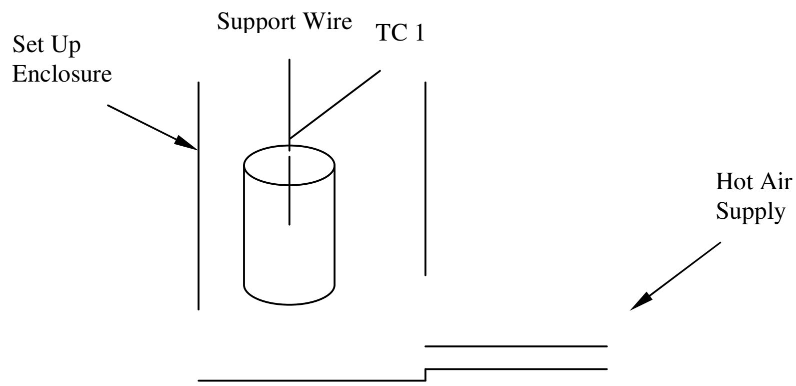

Figure 3.13 - Experimental Set Up Used for Determination of the Internal Chamber Temperature.

A 5400 s long test was performed, with temperature readings taken every 900 s, as shown by the results presented in Figure 3.14.

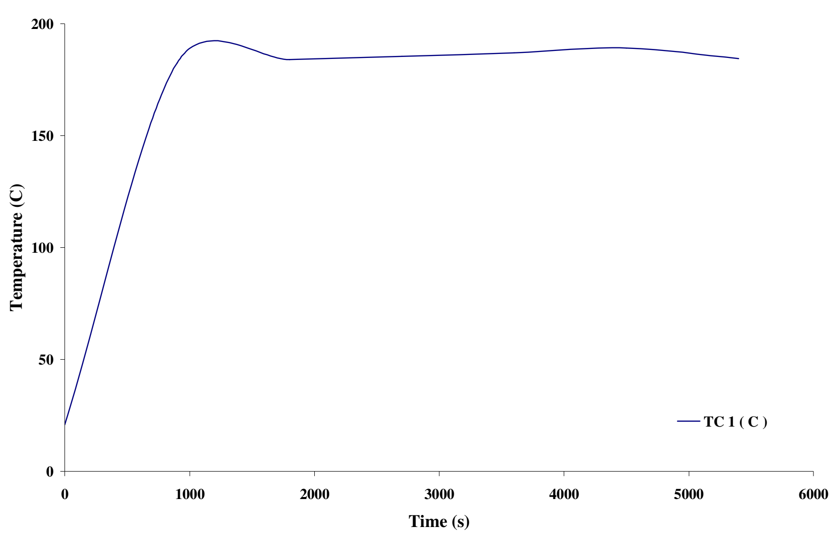

Figure 3.14 - Internal Chamber Temperature.

These results show that constant temperature within the container may be readily attained.

Thus, the next step would be to assess the radial temperature distribution within the internal chamber, to confirm that the temperature gradients between the centre of the internal chamber and possible locations closer to the internal surface of the test vehicle's chamber were small.

Temperature Distribution Within the Internal Chamber

An assessment of the radial temperature distribution within the internal chamber of the test vehicle is of major importance to ensure that on a field trial the whole sample will be submitted to the same level of heating, therefore preventing the induction of timely different reaction zones.

Thermal conductivity of the sample creates already on its own heat transfer gradients that control the reactions leading to Cook-Off, therefore altering the time to explosion. Consequently, it is desirable to eliminate as much as possible any other sources that might induce different reaction rates on different sites of the same sample.

The present test was conducted in a similar set-up as the test described previously, with the following exception: the top end cap had in this case three 1 mm diameter orifices. These aligned orifices were located in the centre (1) and as close as possible of both sides (2) of the end cap (see Fig. 3.15).

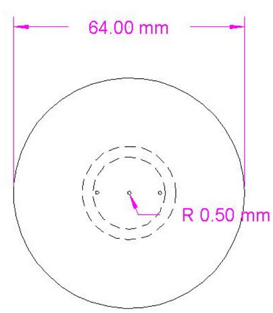

Figure 3.15 - Top End Cap View.

The K-type thermocouples were placed at half height of the internal chamber. Off-the-shelf Araldite was used to simultaneously guarantee the position of the sensors and the sealing of the internal chamber. This epoxy resin, once applied to the top end cap, was allowed to cure for 4 hours in an oven at 473 K.

A 19800 s long test was performed, with temperature readings taken every 900 s. The results are presented below in Figure 3.16.

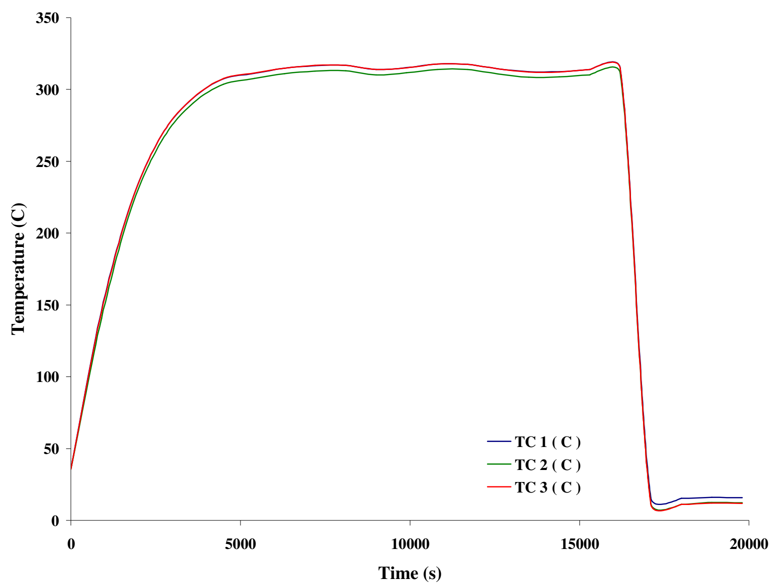

Figure 3.16 - Radial Temperature Distribution of the Internal Chamber of the Cook-Off Test Vehicle.

There is a small temperature gradient with respect to the radial temperature distribution on the Cook-Off test vehicle: the temperature gradient between the wall thermocouples (TC 1 and TC 3) is ≤ 0.2 K and the difference between the temperature at the centre of the empty test vehicle and at the wall is ≤ 4 K.

Top End Cap Temperature

Equally important was to evaluate the top end cap temperature so to confirm that as far as possible all the sample in contact with the inner surface of the test vehicle was kept at the same temperature, in each instant. Using the same basic experimental set-up as previously, a test was run with a K-type thermocouple clamped to the outside of the top cap. In order to be able to establish any comparisons this test was similarly run for 3600 s and temperature readings were taken every 900 s (see Fig. 3.17).

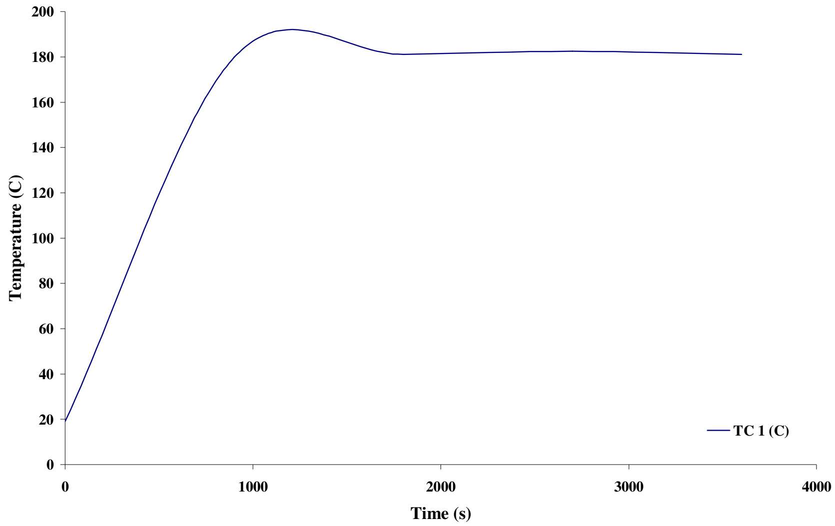

Figure 3.17 - Top End Cap Temperature.

Figure 3.17 demonstrates that at the top end surface of the test vehicle there is a rapid attainment of the required temperature and constancy prevails for long periods of time.

Evaluation of the potential temperature gradients between the centre of the combustion chamber (Test 2) and the top end cap (Test 1) is address by the following graph:

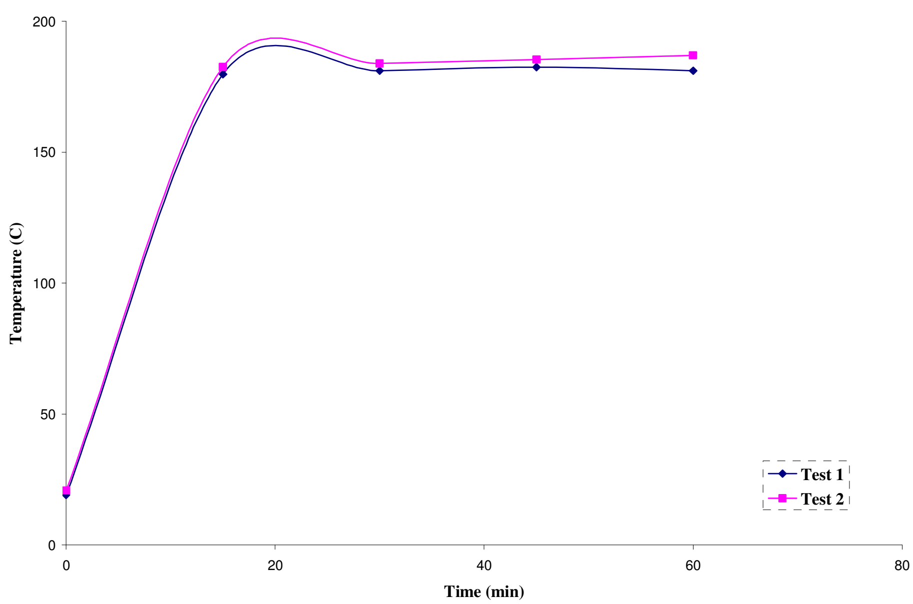

Figure 3.18 - Comparison of Temperature Profiles Obtained for Wall Temperature and Internal Combustion Chamber of the Cook-Off Test Vehicle.

The results demonstrate that for the experimental configuration used there is a temperature gradient, for time intervals of 3600 s, of approximately 0.03%. This value is considered acceptable for the firing programme proposed.

3.2.4. Mechanical Integrity

Tests were performed in order to assess the suitability of the washers used to seal the sample inside the Cook-Off test vehicle.

The original test vehicle configuration was filled with TNT, assembled and placed on an oven at 373 K for 3 hours. Visible examination revealed leakage of molten TNT on the bottom end cap.

It is possible that this was partly due to the hardness of the copper washers, which are not annealed before use. However, significant pitting of the metal, presumably where it had been in contact with molten TNT, suggested that copper was not the most suitable material for this purpose.

Therefore no further work was done with copper and HE 15 aluminium washers were tried: after 66 hours in an oven at 373 K no leakage of TNT was found anywhere in the small scale test vehicle.

Observation of the aluminium washers for signs of corrosion products proved these were not as marked as on the copper washers (cf. corrosion products' analysis).

The aluminium washers proved to be suitable for sealing the sample inside the small scale test vehicle chamber.

3.2.5. Corrosion Products Analysis

Copper and aluminium washers recovered from the mechanical integrity trial described above were examined for corrosion products with a JEOL JSM 840A Scanning Electron Microscope allied to a PGT IMIX Microanalyser. The method of analysis used was Energy Dispersive X-ray (EDX).

The chemical analysis technique involves the detection, by means of an energy dispersive spectrometer (e.g. solid state device that discriminates among X-ray energies), a spectrum of characteristic X-rays that are produced by a sample placed in an electron beam. Peaks that occur in the spectrum are characteristic to particular elements, according to Moseley's Law. From all the electron probe microanalysis (X-rays) methods this is the one that performs best in terms of lateral resolution, but its concentration sensitivity is the poorest, thus making quantitative analysis extremely difficult (Friel, 1998; Pozsgai, 1995). The disadvantages of this technique are that individual elements may have more than one peak associated with them, some peaks from different elements may overlap to a certain degree, and elements with atomic number lower than carbon are not detected. Furthermore, intensity increases with increasing atomic number. Apart from this effect though, a taller peak does not always imply a higher quantity of that element (Kimber, 1999).

The results obtained are shown in Figures 3.19 and 3.20. On Figures 3.21 to 3.24 optical photographs taken from the analysed washers' surfaces are presented. There are no available microscopic photos as these would impose an added coating to the washers' surfaces, and any coating of the surfaces would make it impossible to obtain any further information.

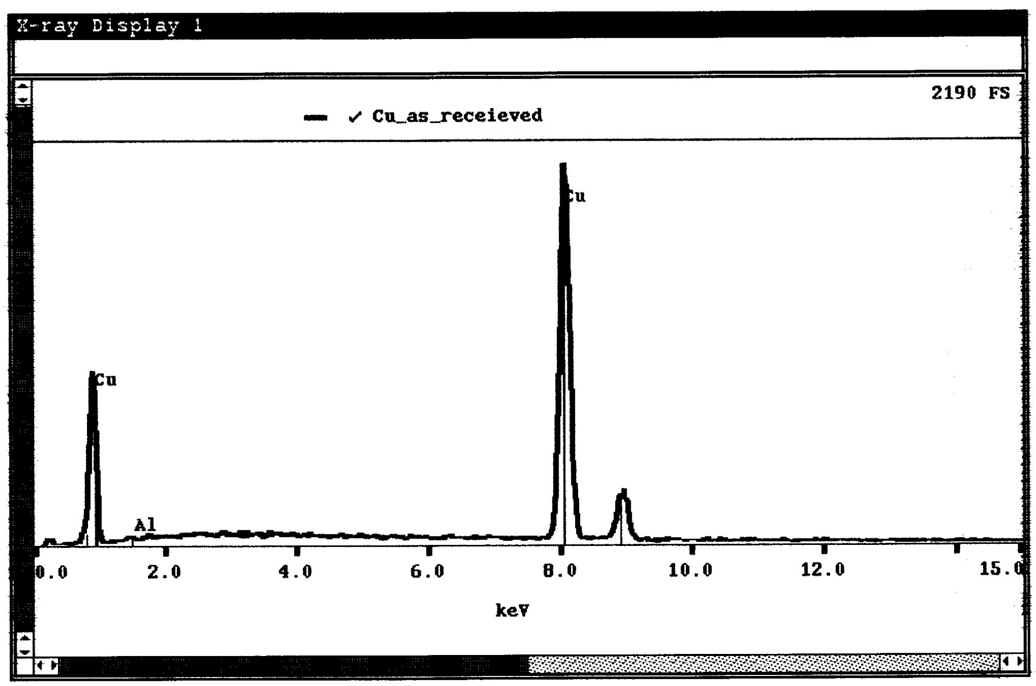

Figure 3.19 - Spectrum of the Copper Washer as Received.

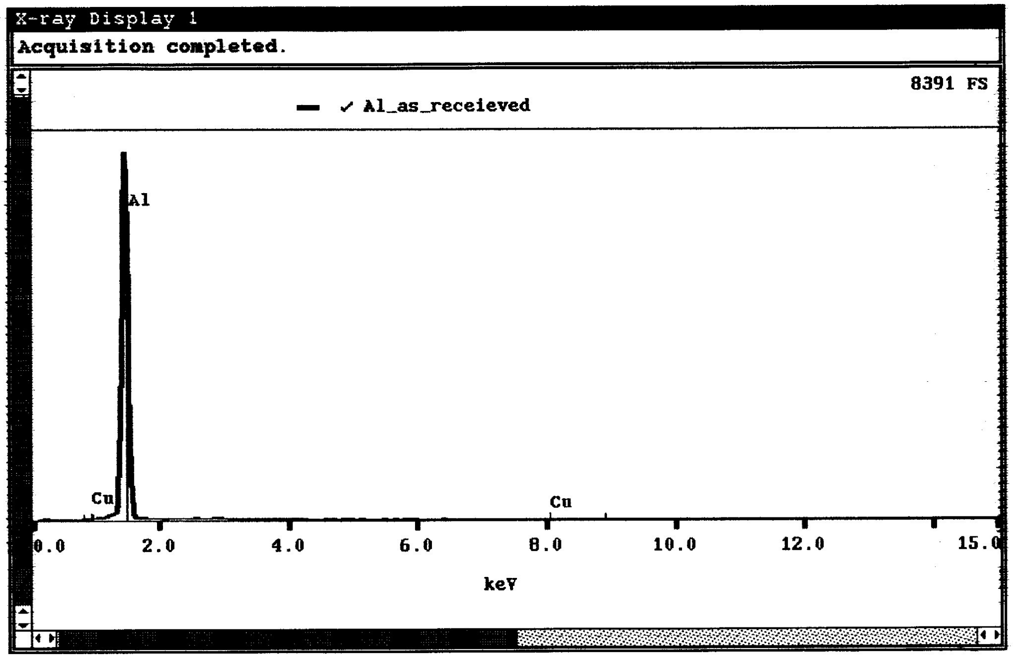

Figure 3.20 - Spectrum of the Aluminium Washer as Received.

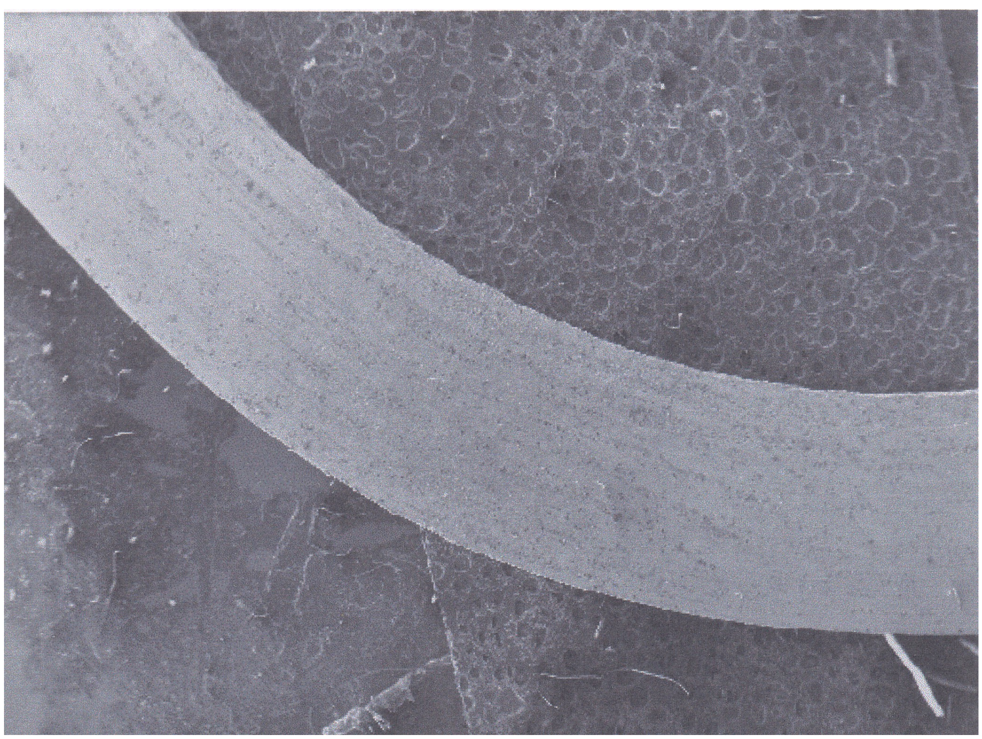

Figure 3.21 - Photo of the Top End Copper Washer.

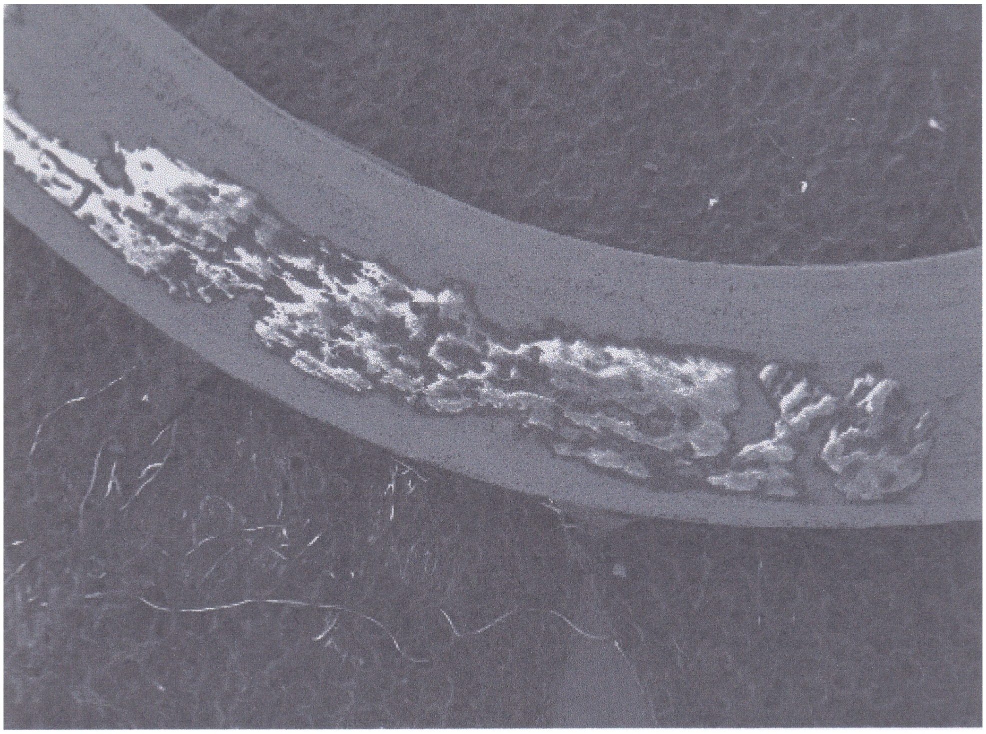

Figure 3.22 - Photo of the Bottom End Copper Washer.

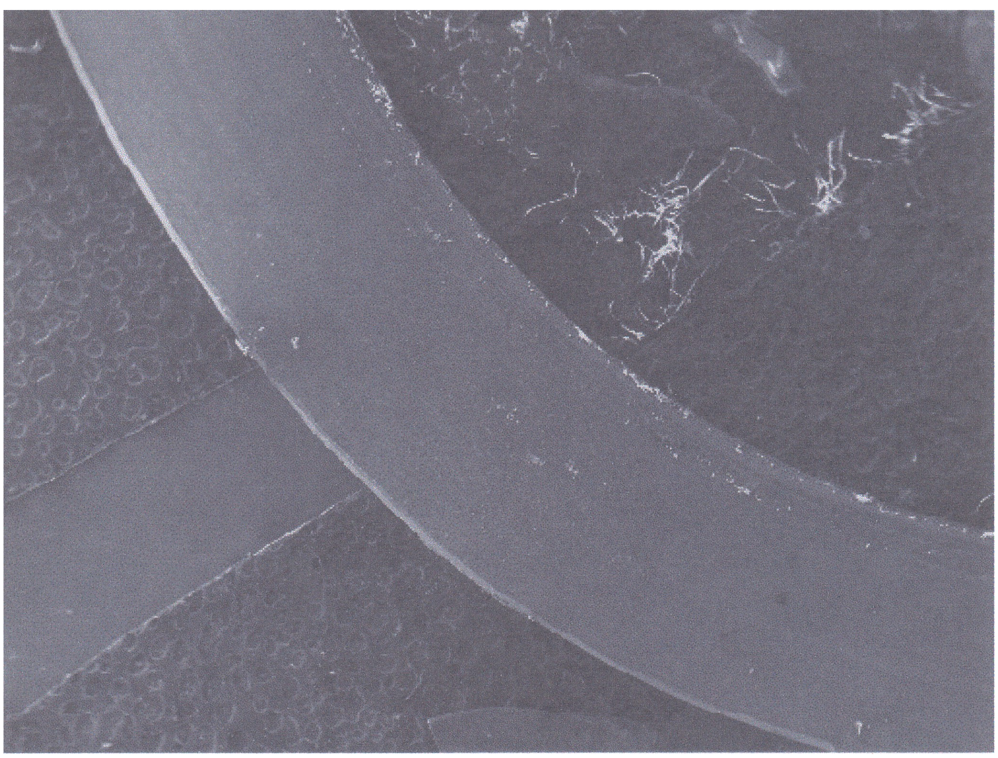

Figure 3.23 - Photo of the Top End Aluminium Washer.

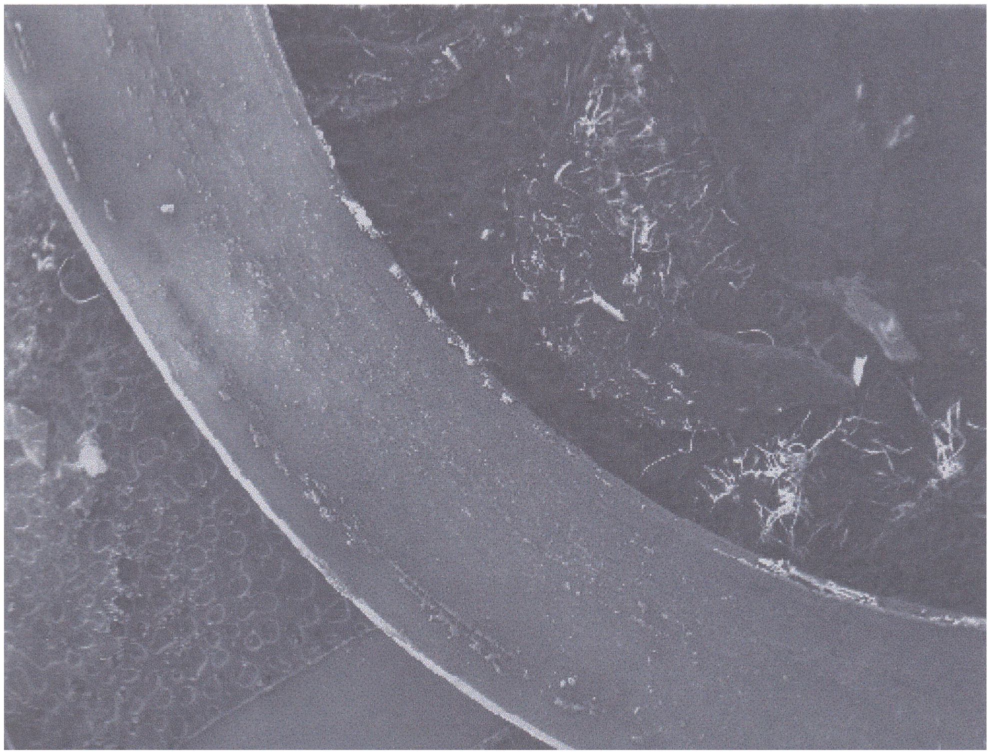

Figure 3.24 - Photo of the Bottom End Aluminium Washer.

Incompatibility of energetic materials (e.g. explosives) with metals has been known to occur as well as between explosives and corrosion products of metals (Rogers, 1975; Němčák & Hanus, 1995).

3.2.6. Preliminary Field Trials

Field trials were necessary to assess structural behaviour of the small scale test vehicle in response to the violence of the event, as well as the test vehicle confinement and the suitability of the data acquisition systems selected.

Two field trials were performed to assess the structural behaviour of the test vehicle and simultaneously the data acquisition system: Fast Cook-Off test on a TNT and a 75RDX/25TNT filled small scale test vehicles.

The same experimental set-up was used for both trial vehicles: a heating cord system, Eurotherm Mark 1, attached to the outer surface of the test vehicle wall, which provided variable heating rates and temperatures, when connected to a 220 V variable voltage Variac. In these trials the Variac was set at 20 V. A K-type thermocouple was placed at the outer surface of the test vehicle clamped against the wall by the heating cord. A K-type extension was used to connect the measuring thermocouple to a 1200 Series (12-Bit) Squirrel Meter/Logger used to record the trial's temperature profile on a control room adjacent to the firing chamber. This heating system was used just for simplicity reasons for setting up a field trial.

In the case of the TNT filled test vehicle it was not possible to record the measured temperatures due to an instrument fault. Nevertheless, results concerning the violence of response of the event and the structural damage of the vehicle were collected (see Figs. 3.25 - 3.27).

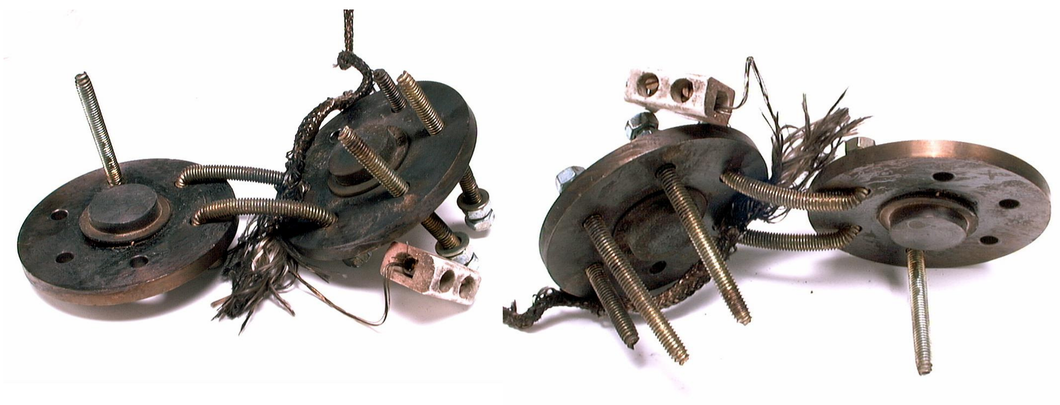

Figure 3.25 - Recovered TNT Filled Small Scale Test Vehicle.

Figure 3.26 - Damage Induced to the End Caps.

Figure 3.27 - Damage Induce to the Stand of the Test Vehicle.

It is expected that TNT would produce the least violent response of the planned samples and it was therefore decided to add a thick plastic base to the bottom of the operational configuration of the test vehicle to minimise possible damage to the fragment containment box.

The 75RDX/25TNT filled test vehicle was expected to represent the worse possible violence of response scenario of the mixtures of RDX/TNT considered in this study.

The results collected are presented in Figures 3.28 to 3.30.

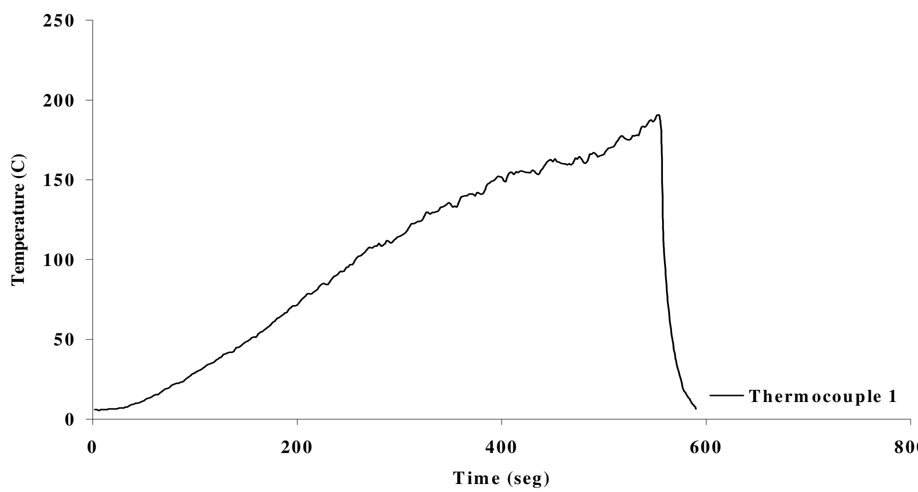

Figure 3.28 - Fast Cook-Off Profile for a 75RDX/25TNT Small Scale Test Vehicle.

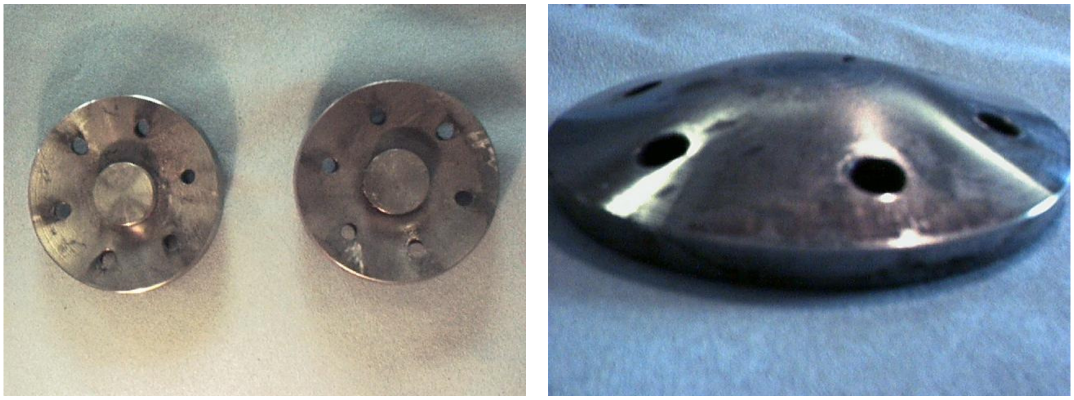

Figure 3.29 - Damage Induced to the End Caps.

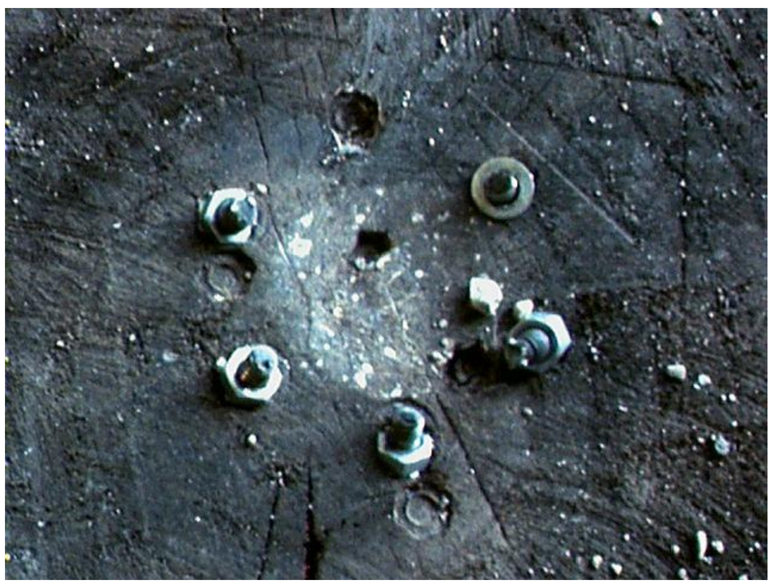

Figure 3.30 - Damage Induced to the Stand of the Test Vehicle.

No fragments of the body were recovered, with the exception of the following remains of bolts, nuts and washers (see Fig. 3.31):

Figure 3.31 - View of the Remains Recovered from a 75RDX/25TNT Filled Test Vehicle.

Another trial was conducted on an instrumented small scale test vehicle to assess the functioning of the thermocouples inside the test vehicle chamber and allow the retention of the confinement of the operational configuration of a test vehicle. A small scale test vehicle filled with TNT was fitted with three K-type thermocouples inserted into three screw + metallic ferrules assemblies in drilled orifices in the top end cap of the test vehicle (see Fig. 3.32).

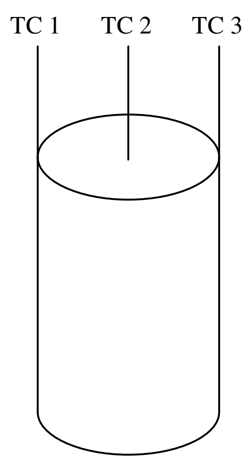

Figure 3.32 - Schematic Representation of the Test Vehicle Assembly.

The results recorded with the data acquisition system are presented in Figure 3.33.

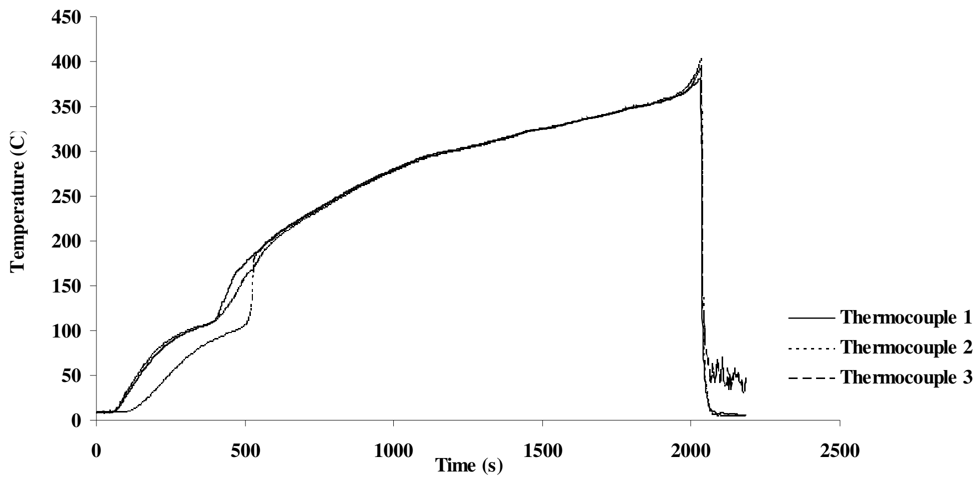

Figure 3.33 - Temperature Profile of a Fast Cook-Off Trial of a TNT Small Scale Test Vehicle with 3 Ferrules.

A *post mortem* analysis revealed that there was a venting type of response to the fast heating profile, caused by the rise in pressure inside the vehicle's chamber and a spray of molten TNT with simultaneous thermocouples' expulsion from the test vehicle (see Figs. 3.34 and 3.35).

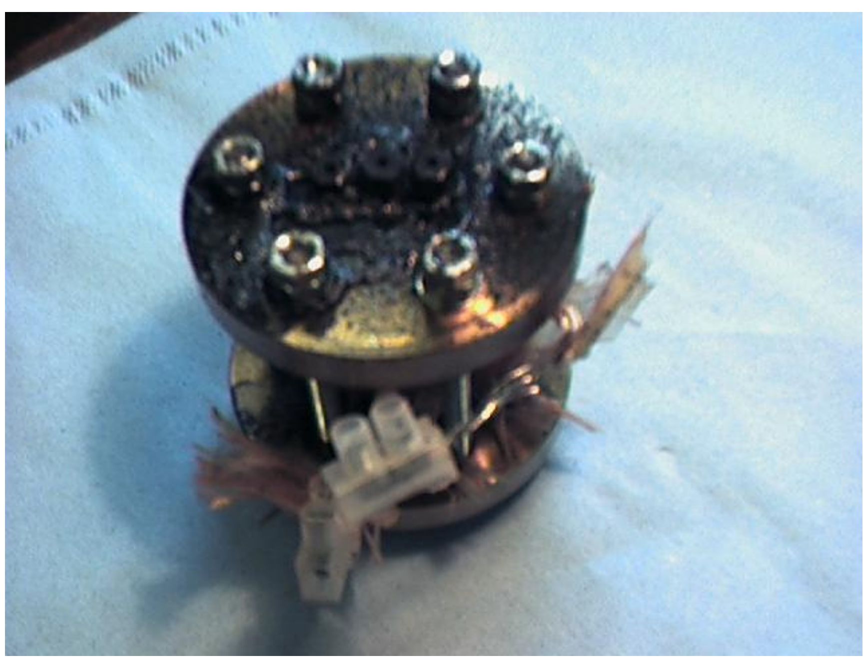

Figure 3.34 - Instrumented TNT Filled Small Scale Test Vehicle.

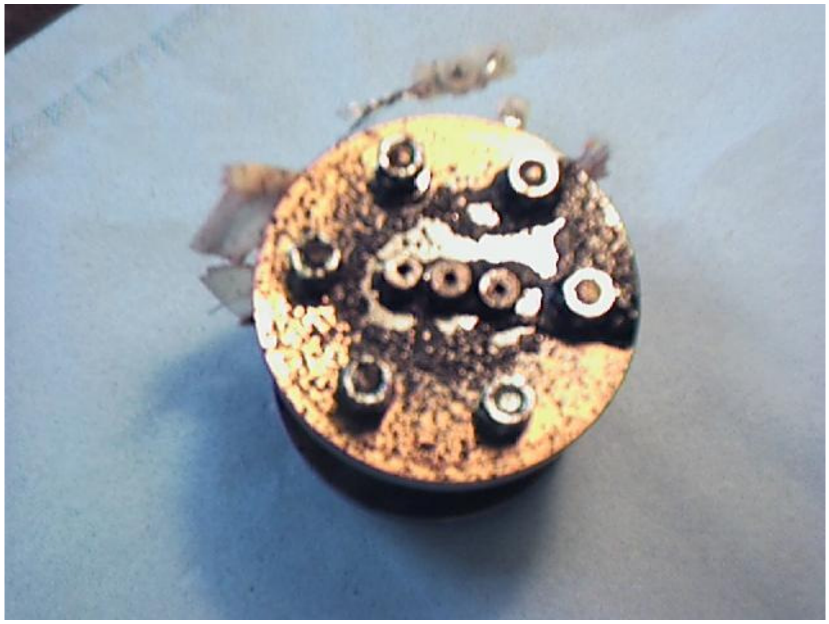

Figure 3.35 - Top End Cap Detail.

Further preliminary Cook-Off tests performed with the hot air heating system proved this system to be completely unsuitable for the experimental set-up designed for this firing program, due to two main reasons: fragment containment box was acting as a heat sink and the impossibility of efficiently insulating the containment box from the weather conditions effects on the ambient conditions inside the firing chamber. Also the heating element of this system suffered systematic rupture of its integrity due to the extreme temperature gradients between tests caused by the weather conditions, making this a very expensive facility to maintain.

3.2.7. Small Scale Test Vehicle - Operational Configuration

EN3 low Carbon mild Steel was selected for the test vehicle, because it is readily available, is of low cost and provides adequate performance (BS 970:1955 % C = 0.25 max; % Si = 0.05/0.35; % Mn = 1.00 max; % S = 0.060 max; % P = 0.060 max).

Although the design had proved satisfactory, it was decided to increase the thickness of the end caps to avoid any possible distortion during sealing: the 64 mm diameter end caps were increased in thickness (6 mm flange and 8 mm centre).

It was decided to keep six sister 5 mm bolts to hold together the test vehicle. As for the 5 mm studding used for the bolts a chrome protected mild steel was chosen and 5 mm washers and nuts were bought off-the-shelf.

Similarly, the screw and ferrule assembly suffered some improvements. The use of ferrules is justified by the concern in preventing any air or liquid leakage. PTFE was selected for their manufacture, because it softens slightly at high temperature and moulds itself into the space available, which was made as small as possible. These ferrules had a diameter just enough to allow the thermocouple through in order to prevent the system from venting (see Fig. 3.36).

The screws for these units were bought off-the-shelf from Swagelock (ref. Male Nuts SS-1F2-1GC).

Instrumentation for thermal profile capture was reduced to a maximum of two K-type thermocouples (one in the centre of the sample and another one close to the wall of the chamber in the same height alignment). Therefore, the test vehicle comprised two permanent openings for each set of ferrule assembly + thermocouple.

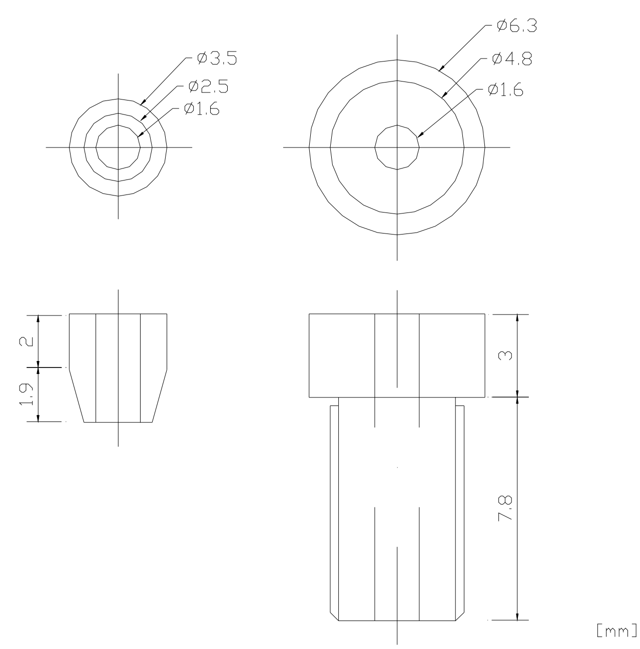

Figure 3.36 - Assembly Ferrule and Screw.

It is significant to note that the internal chamber was designed with zero ullage, as it was assumed a non-existent increase in the volume of any samples containing TNT, after these have been submitted to temperature and undergoing melting, as some authors state this design feature in their vehicles.

Following the specifications on Figure 3.37, the small scale Cook-Off test vehicles were constructed at the Mechanical Workshops – Technical Support Services at the Royal Military College of Science/Cranfield University.

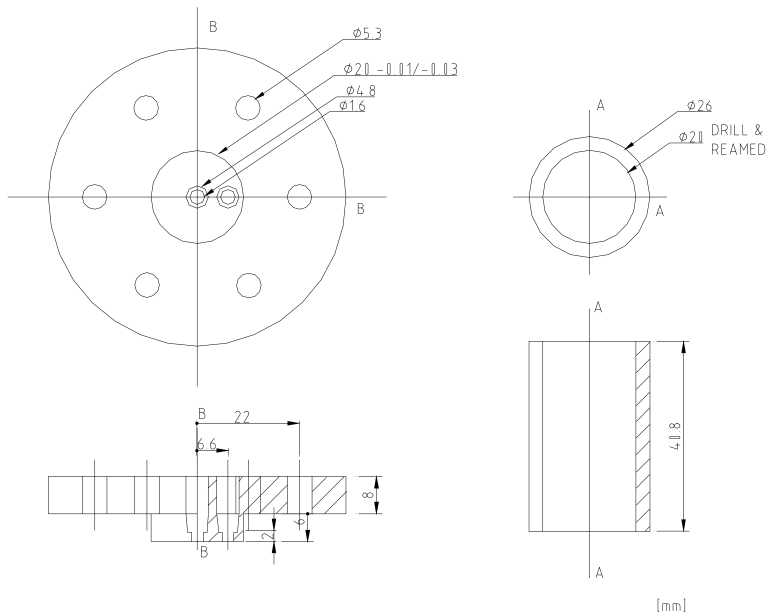

Figure 3.37 - Small Scale Cook-Off Test Vehicle.

3.3. DESIGN & CONSTRUCTION OF A MEDIUM SCALE COOK-OFF TEST VEHICLE

A medium scale test vehicle, with a 0.20 kg capacity, was designed and constructed. The effect of scale study proposed requires that all the Cook-Off parameters, exception made for the dimensions of the tested vehicles, are kept constant. Accordingly, the material selected for the medium scale Cook-Off test vehicle was the same EN3 low Carbon mild Steel as used for the small scale test vehicles. The bolts, nuts and washers although differing in dimensions were of the same materials and manufacturer as the ones for the small scale test vehicles.

The preparation of the medium scale test vehicles followed the same procedures used for the small scale test vehicle preparation of the test samples and the subsequent Cook-Off testing procedures were also maintained unaltered.

3.3.1. Medium Scale Test Vehicle

A medium scale test vehicle was design incorporating the scaling up proposed for this study (see Fig. 3.38).

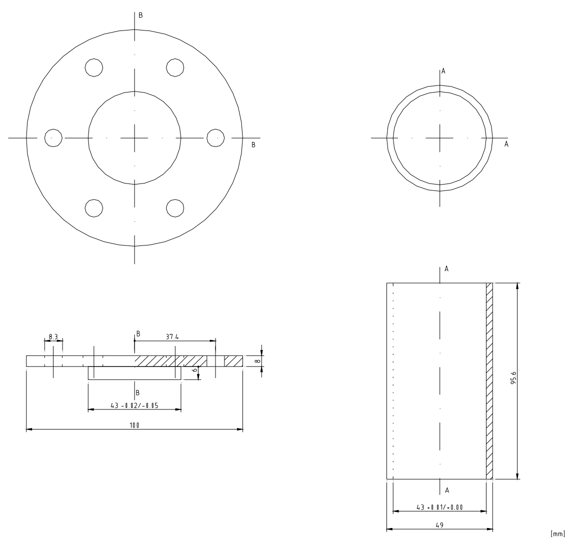

Figure 3.38 - Medium Scale Test Vehicle.

This design was evaluated by performing the following preliminary tests:

- Mechanical Stress;
- Mechanical Integrity.

3.3.1.1. Mechanical Stress Failure Tests

The Houndsfield tensometer could not accommodate the larger bolts used for the medium scale, and therefore both sizes were tested using an Instron Universal Testing Machine. Two different series of stress failure tests were performed to allow comparison of results between small and medium scale:

(i) Various combinations of nuts on single bolts were tested to induce failure on the shank of the bolt and not on the nut threads;

(ii) Completely assembled test vehicles were tested at room temperature and at high temperature, to assess any effect on the failure mode.

The results obtained for bolts with various combinations of nuts (single or double at each end, single at one end and double at the other) are shown in Table 3.II:

Nuts' Configuration	Stress Failure (MPa/bolt) Small Scale	Stress Failure (MPa/bolt) Medium Scale
1 + 1	454	468
1 + 2	475	----
2 + 2	480	468

Table 3.II - Experimental Results Obtained for Stress Failure for Small and Medium Scale Bolts.

The results for completely assembled test vehicles at room and elevated temperature are presented in Table 3.III:

	Small Scale		Medium Scale	
	T_{room}	$T_{523\ K}$	T_{room}	$T_{523\ K}$
Maximum Load (kN) Possible from all Six Bolts	55	57	138	137
Pressure to Fail (kbar)	22	29	29	29

Table 3.III - Experimental Results Obtained for Stress Failure for Small and Medium Scale Completely Assembled Cook-Off Test Vehicles, at Different Temperatures.

3.3.1.2 Mechanical Integrity of the Test Vehicles

The following procedure was adopted to test for leakage of molten TNT.

The filled vehicle was assembled with the nuts tightened in diagonal sequence to the appropriate torque and thereafter:

(i) The vehicle was placed on a Petri dish, in an oven at 373 K for 66 hours;

(ii) The vehicle was checked every 900 s for the first hour and every hour for the next three hours and then at the end and start of every working day;

(iii) If leakage was observed the oven was switched off and allowed to cool to room temperature. When the sample had cooled to less than 323 K it was removed from the oven and placed in the breakdown facility for disposal.

Caution should be exercised when performing this test, as TNT has been reported to undergo violent thermal degradation under similar test conditions (Scholtes, 2001).

Aluminium was tried successfully in the small scale vehicle, but reproducible sealing could not be achieved at medium scale: two possible types of finishing of the aluminium washers were tested – drilled + reamed from aluminium solid bar (see Fig. 3.39) and polished from aluminium tube (see Fig. 3.40).

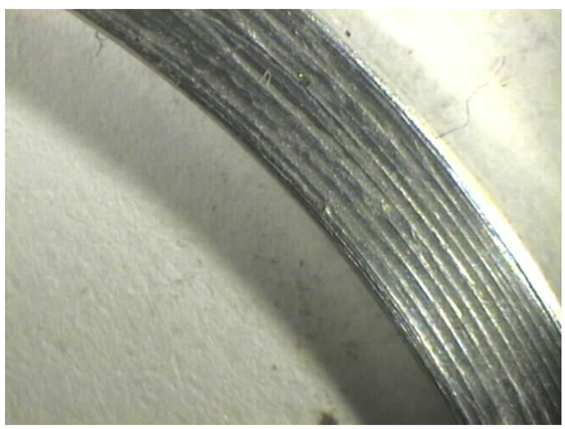

Figure 3.39 - Washer Manufacture from Drilled + Reamed Aluminium Solid Bar.

Figure 3.40 - Washer Manufacture from Aluminium Tube - Polished Finishing.

In both cases it was proved these finished surfaces were providing leakage pathways to molten TNT. The mechanical integrity tests also proved the significant role of other factors influencing the sealing of the test vehicle: length of the bolts, use of bolt washers, positioning of nuts, closure procedure and torque applied.

A satisfactory compromise was achieved between all these factors, and the remaining leakage was attributed to the finishing of the surfaces. Therefore, steps were taken to eliminate metal washers from the main body of the Cook-Off test vehicle.

The most satisfactory results were found with internal combustion engine head gasket seals. This material was selected due to its readily availability, low cost and thermal characteristics.

Several thermal characterisation tests were performed in order to assess the suitability of this material to the firing program proposed for this study: at constant temperature of 558 K, as this was the limit temperature the available oven would allow, and at ramped temperature up to 558 K. In both cases the material withstand the temperature profiles selected therefore allowing for further use in the Cook-Off firings programmed. The mechanical integrity test procedure described above was then used to test TNT filled Cook-Off test vehicles assembled with internal combustion engine head gasket seals. The results proved satisfactory and a decision was made to use this type of seals for the rest of the programme.

Once the problem of liquid leakage was solved, the vehicles had to be made air tight as the thermocouples assembly was an impediment to it. The ferrule and screw assembly through which the braided leads of the K-type thermocouples passed were rendered completely air tight using an explosively compatible long curing epoxy resin system.

3.4. SELECTION AND PREPARATION OF THE TEST SAMPLES

In this section the selected materials to be tested will be described as well as the procedures for preparation and formulation of the test samples. The test samples were submitted to thermal analysis and the experimental procedures and results will be presented. As a final stage of preparation of the test samples procedures of filling of the test vehicles are explained as well as the quality control assessment.

3.4.1. Characterisation of the Test Samples

The compounds selected as test materials for this study were RDX and TNT. A brief description of the composition and formulation procedures of the explosives systems under study is presented below as well as a thermal analysis study of the test samples.

3.4.1.1. Test Samples – Composition and Formulation

The single explosives RDX and TNT were standard UK military grades obtained from Royal Ordnance Bridgwater, United Kingdom.

The RDX used was Recrystallised Batch C5562 Consignment No. 2661. RDX was submitted to a 3 hours drying operation at 373 K before being used for DSC/TGA analysis or for the preparation of the mixtures with TNT.

The TNT received was flake TNT (set point 353.6 K) and was used as received.

The samples selected to be under investigation in this study are presented in Table 3.IV:

Composition (wt %)	Composition (wt kg)
100 RDX	0.02 RDX
75:25 RDX/TNT	0.015/0.005 RDX/TNT
60:40 RDX/TNT	0.012/0.008 RDX/TNT
50:50 RDX/TNT	0.01/0.01 RDX/TNT
40:60 RDX/TNT	0.008/0.012 RDX/TNT
25:75 RDX/TNT	0.005/0.015 RDX/TNT
100 TNT	0.02 TNT

Table 3.IV - Explosive Samples Tested in Small and Medium Scale Cook-Off Studies.

Homogeneous mixtures of RDX and TNT for thermal analysis were prepared by stirring together weighed amounts of the ingredients in a glass beaker heated on a water bath at 373 K. When the slurry appeared homogeneous it was poured in small increments into a second, cold beaker, allowing the cast to solidify before further addition.

3.4.2. Thermal Analysis Study

Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA) were performed on the test samples submitted to Cook-Off.

3.4.2.1. Differential Scanning Calorimetry

The equipment used for the DSC measurement was a Mettler TA 4000 system with a TC 11 TA Process Control Unit and a series of measuring cells. This equipment allows other than DSC measurements: ThermoGravimetric Analysis (TGA) and Thermo-Mechanical Analysis (TMA) runs.

The DSC measurements were recorded, using shallow aluminium crucibles either sealed or unsealed at a constant heating rate of 10 K/min.

Measurements were taken between 303 K and 673 K and the furnace was allowed to cool down to room temperature before a new sample was introduced.

Sample size was limited to 2.5 x 10^{-6} kg to minimize damage to the equipment in the event of a violent reaction.

The results obtained for test samples with DSC measurements, under confinement and no confinement conditions, are presented in Table 3.V below:

Sample (% RDX)	T_{peak} (K)	Onset (K)	ΔH (J/g)	T_{peak} (K)	ΔH (J/g)	ΔHu (J/g)	T_{peak} (K)	T_{peaku} (K)	ΔH (J/g)	ΔHu (J/g)
100	477	475	121	513	2503	2509				
75	355	351	38	511	2374	2151				
60	355	351	38	510	2641	2041				
50	355	352	50	513	1992	1993	549		162	
40	355	351	79	510	852	826	576	537	874	3.5
25	354	351	97	511	492	272	580	549	948	73.2
0	353	352	96	--	--	--	599	322	1544	281.5

u - unconfined

Table 3.V - Peak Temperatures and Enthalpies DSC Measurements.

The thermal analysis profiles in Figures 3.41 and 3.42 show the results obtained for pure explosive compounds RDX and TNT, respectively, under confinement conditions.

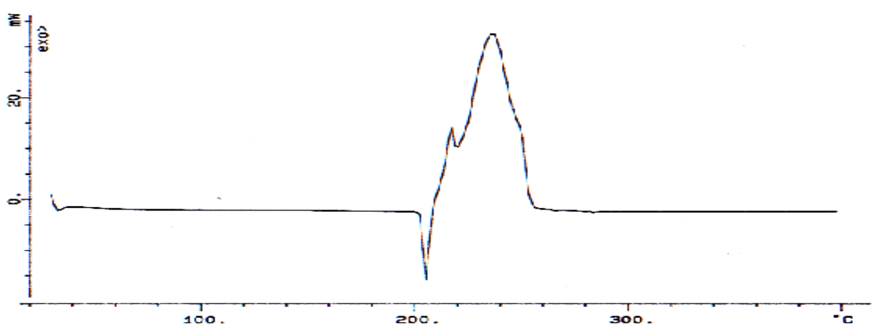

Figure 3.41 - Thermal Analysis Profile for RDX.

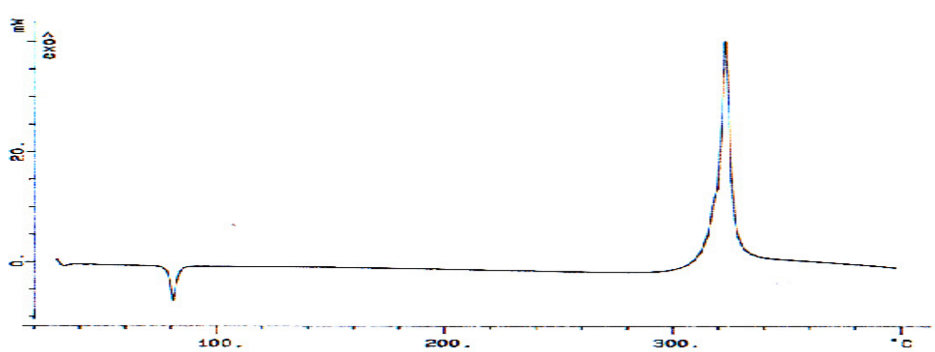

Figure 3.42 - Thermal Analysis Profile for TNT.

In Figure 3.43 are presented the thermal analysis profiles concerning the DSC measurements of the RDX/TNT mixtures, under confinement conditions.

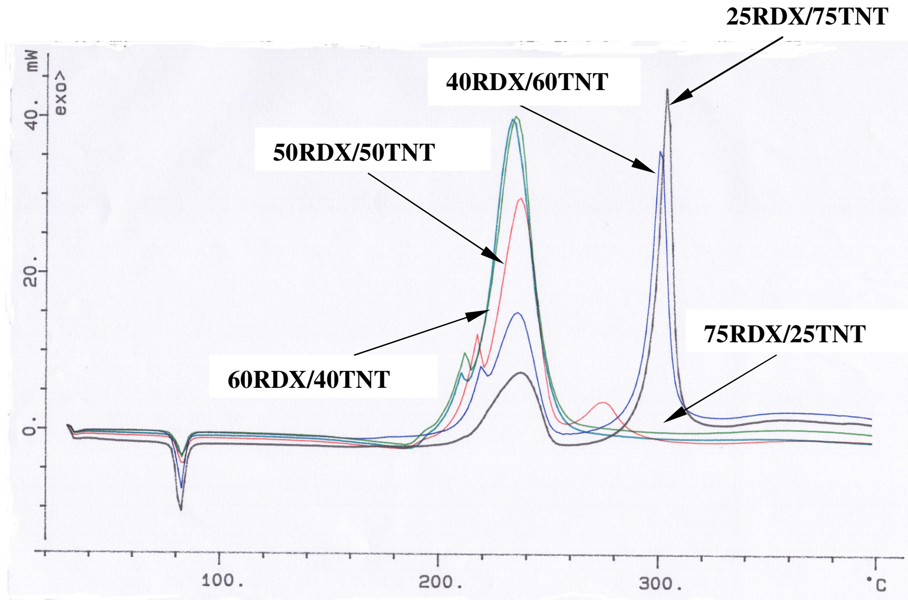

Figure 3.43 - Thermal Analysis Profiles for RDX/TNT mixtures.

3.4.2.2. Thermogravimetric Analysis

The equipment used for the TGA measurement was a Mettler TA 4000 system with a TC 11 TA Process Control Unit and a series of measuring cells. The samples were contained in reusable ceramic crucibles, from 303 K - 673 K, heated at a constant rate 10 K/min, in an atmosphere of either air or nitrogen. After every measurement, the furnace was allowed to cool down to atmosphere temperature, before a new sample was introduced.

The results obtained for the TGA studied samples, under normal and nitrogen atmospheres, are presented in Table 3.VI:

	Air Atmosphere				Nitrogen Atmosphere			
	Mass (mg)	**D_{peak} (K)**	**Residue C (%)**	**Residue C (%)**	**Mass (mg)**	**D_{peak} (K)**	**Residue C (%)**	**Residue C (%)**
(%RDX)								
100	8.015	502.5	95.18	4.68	6.198	513.5	96.32	3.53
75	3.382	502.5	--	11.71	4.243	504.0	--	10.18
60	5.781	502.5	--	14.41	12.270	498.0	--	10.66
50	4.520	499.5	--	18.46	10.767	483.0	--	17.31
40	6.168	504.0	--	21.99	10.844	502.5	--	21.91
25	3.482	502.5	--	6.78	5.003	471.0	38.55	16.36
0	11.872	676.0	--	12.61	12.688	571.5	29.64	2.18

Table 3.VI - Residues from TGA Measurements.

On the thermal analysis curve presented below the thermal degradation undergone by RDX, RDX/TNT mixtures and TNT, under a normal atmosphere, is shown.

Notice that the degradation process for the TNT indicated in Figure 3.44 takes longer to occur than in any other explosive system.

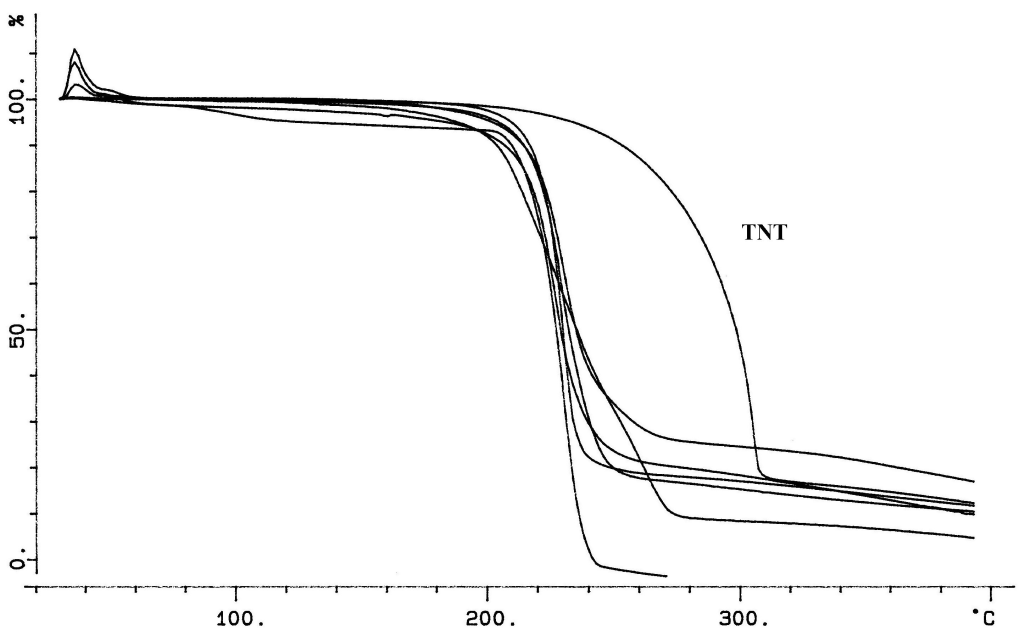

Figure 3.44 - Thermal Analysis Curve for RDX, RDX/TNT Mixtures and TNT, under a Normal Atmosphere (mass % vs. degrees Celsius).

3.4.3. Preparation of the Cook-Off Test Vehicles

The preparation of the test Cook-Off vehicles followed very rigid procedures performed with high accuracy and all the procedures were equally applied to both small and medium scale test vehicles. A thorough description of the sequence of these procedures is presented below:

- the test vehicle components were all thoroughly cleaned with acetone against any possible contamination;

- the top cap was assembled by correct placement of the arrangement comprising two K-type thermocouples with the PTFE ferrules and the correspondent screws;

- it was ensured that the thermocouples were positioned at half height of the available volume to be occupied by the sample and perfectly aligned in relation to each other;

- once the above mentioned arrangement was precisely positioned, the screws were screwed tightly with a spanner, ensuring this arrangement would withstand the maximum pressure possible during the test;

- during the above procedure, the position of the thermocouples was confirmed by means of a micrometer;

- the end caps washers were cut to size and fitted in the end caps, ensuring the most tight fit possible;

- the body of the test vehicle was fitted with the top end cap and the whole arrangement placed in a stand inverted in order to ensure the integrity of the thermocouples during the filling procedure (see Fig. 3.45);

Figure 3.45 - Test Vehicle in Filling Procedure Stand.

- all Cook-Off test vehicles were filled with the required RDX/TNT mixtures by an incremental filling technique to minimise porosity and piping caused by TNT shrinkage on solidification. A pre-weighed quantity of the explosive mixture was melted on a steam bath at 373 K and poured incrementally into the inverted trials vehicle at room temperature, the cast being allowed to solidify between increments. The viscosity of the mixture containing 75% RDX was such that preheating of the vehicle to about 333 K was necessary to allow adequate flow. Filling continued until a level of 1 mm below the face of the assembled bottom end cap.

Pure RDX was filled by simply pouring it in to the vehicle, vibrating the vehicle until the solid has settled, and loading more until the required height was achieved;

- once the filling of the test vehicle was completed, the charge was removed into storage, with the bottom end loose (in order to eliminate any confinement in case an accidental event would arise while in storage) under temperature and humidity controlled conditions until the firings took place.

X-Ray Examination of Filled Test Vehicles

Several attempts were made, with several different equipments, to locate the thermocouples junctions and detect defects (cracks and inclusions) in the filling. Although this is routine industrial practice, success was very limited with the equipment available, and the matter could be pursued no further.

Golden Engineering Inc. (USA) Portable Inspector XR 200

This equipment was used to produce X-rays print of an empty vehicle and a RDX/TNT mixture filled vehicle, so that by comparison it would be possible to extract the most information concerning any filling defects of the charge and the location of the thermocouples junctions.

As resolution can be controlled by selection of the pulse, as each pulse has a standard pulse output, attempts to get the right resolution were made with different pulses (50, 75 and 99 pulses). As demonstrated in Figures 3.46 and 3.47 the resolution at 99 pulses was still insufficient to gain any information on the filling characteristics and as for the thermocouple junctions' locations these were barely visible.

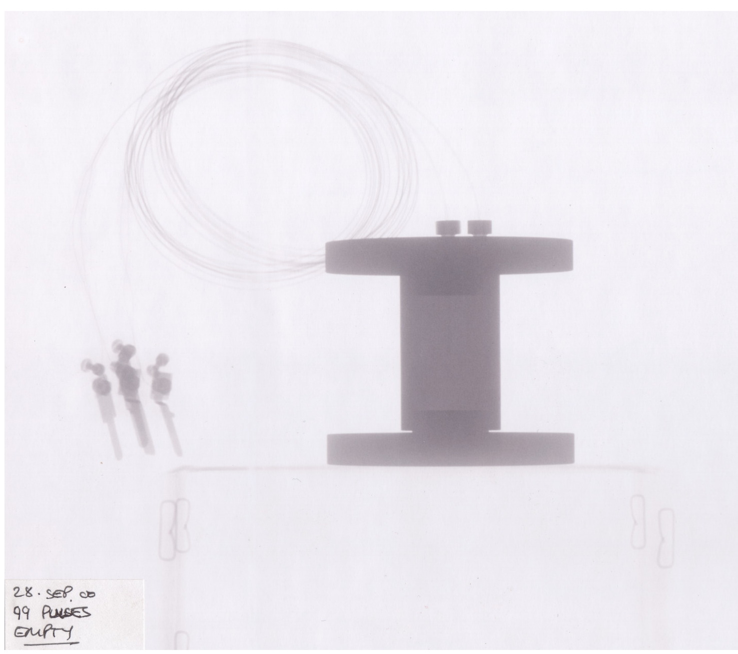

Figure 3.46 - X-Rays Profile of an Empty Charge at 99 Pulses.

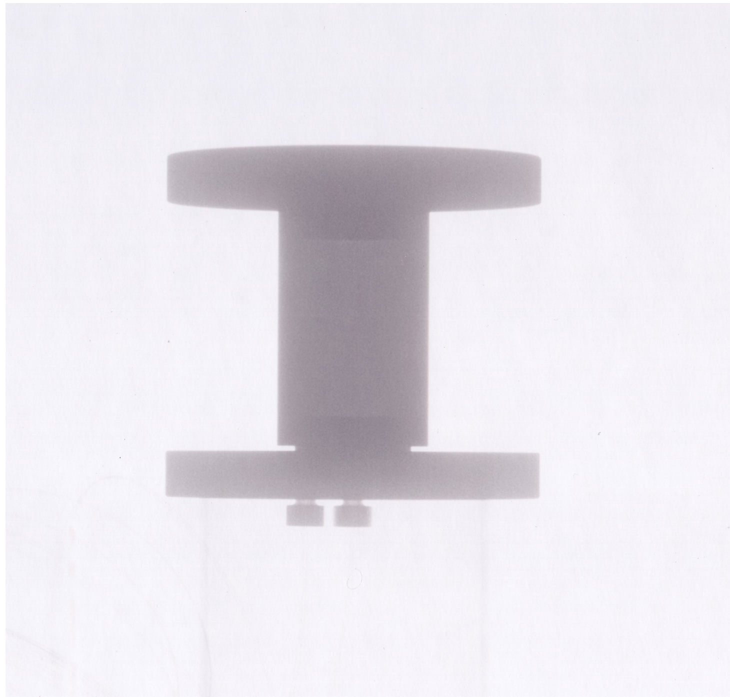

Figure 3.47 - X-Rays Profile of an RDX/TNT Charge at 99 Pulses.

Pantax 250 kV Industrial X-Ray

The same small scale test vehicles were taken into the Rutherford Laboratory of the Department of Materials and Medical Sciences, at the Royal Military College of Science/Cranfield University, in order to perform some X-rays with this industrial equipment. The starting experimental conditions were: 120 kV at 1 mA/15 s and 1 m Film to Focus Distance (FFD). Several others FFDs were tried with no much more success than with the previous technique (see Fig. 3.48).

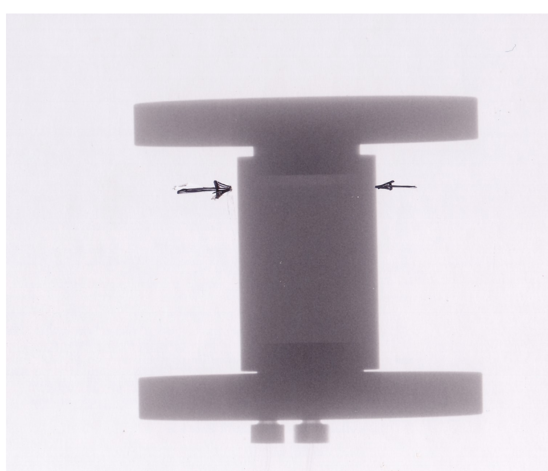

Figure 3.48 - X-Rays Profile of an RDX/TNT Charge at FFD = 2 m.

Philips Medical Systems Super CP 50

This equipment is usually used for radiographic studies on humans, at the Centre for Radiographic and Medical Studies – Department of Materials and Medical Sciences at the Royal Military College of Science/Cranfield University.

The initial experimental conditions were 95 kV and 20 mAs. Other attempts to get a better resolution of the X-Ray profiles obtained led to the use of higher power outputs: 110 kV and 125 kV. The results showed in all cases an insufficient resolution as presented in Figure 3.49.

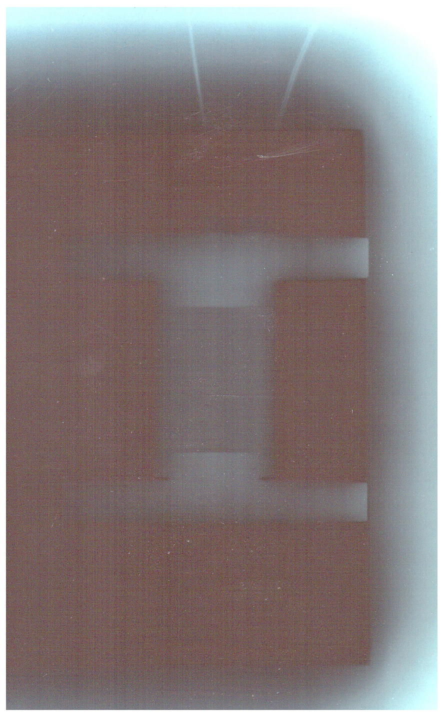

Figure 3.49 - X-Ray Profile of a RDX/TNT Charge at a 125 kV.

The final stage of preparation of a test vehicle (see Fig. 3.50) prior to any Cook-Off test is the fitting of the bottom end cap. Note that all cases particular care was taken to ensure all mating surfaces, particularly the screw threads, were freed from explosive.

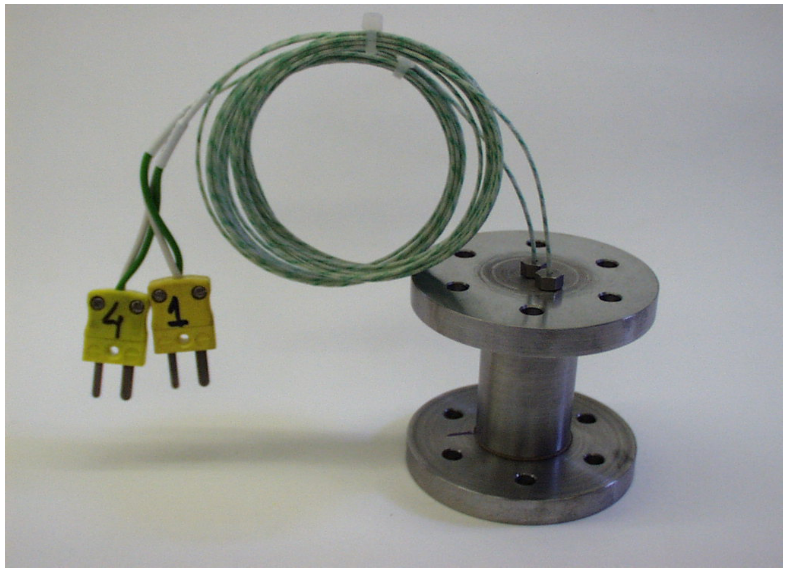

Figure 3.50 - Small Scale Test Vehicle Before Sealing Procedure.

The sealing of the vehicles required a very accurate sequence of procedures and was made according to the design of the vehicle (interference fitted with an internal combustion engine head gasket washer, application of the studding, washer and a two nuts configuration – see Fig. 3.51).

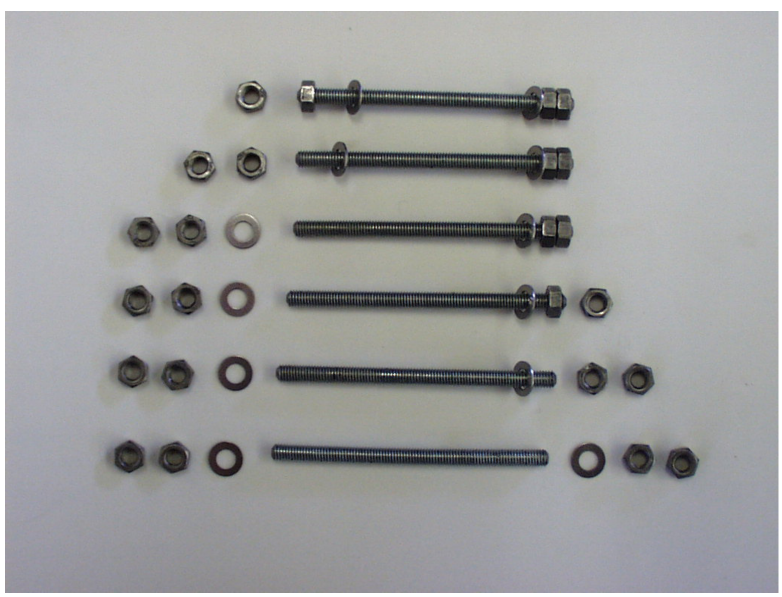

Figure 3.51 - Configuration of Bolts, Washers and Nuts on the Sealing Procedure of the Small Scale and Medium Scale Test Vehicles.

The next stage was the application of a considerable amount of a long curing epoxy resin (explosive compatible Araldite) on the base of the thermocouples, on the top end cap, as an assurance that the test vehicle was air-tight (see Fig. 3.52).

Figure 3.52 - Air-Tight Cook-Off Test Vehicle.

The placement of the heating element and the simultaneous positioning of the external wall control K-type thermocouple followed. This thermocouple was as well position at half height of the test vehicle and in alignment with the two internal thermocouples. As the retention of the sensor's location is of crucial importance as mentioned previously, a wire fixed very tightly to the heating wire in three different locations guaranteed no displacement of the sensor would occur during the cook-off test procedures. The sequence of this procedure is shown below (Fig. 3.53).

Then a closing pressure was applied on each nut end using a torque wrench and a diagonal closing procedure:

- small scale test vehicles: 0.276 kg m;

- medium scale test vehicles: increasing from 0.267 to 0.693 kg m.

These operations were always double checked to certify that none of the nuts had slackened while the diagonal closing procedure was taking place.

The vehicle was then thermally insulated externally with rock wool to reduce heat loss during the experiments (Fig. 3.54).

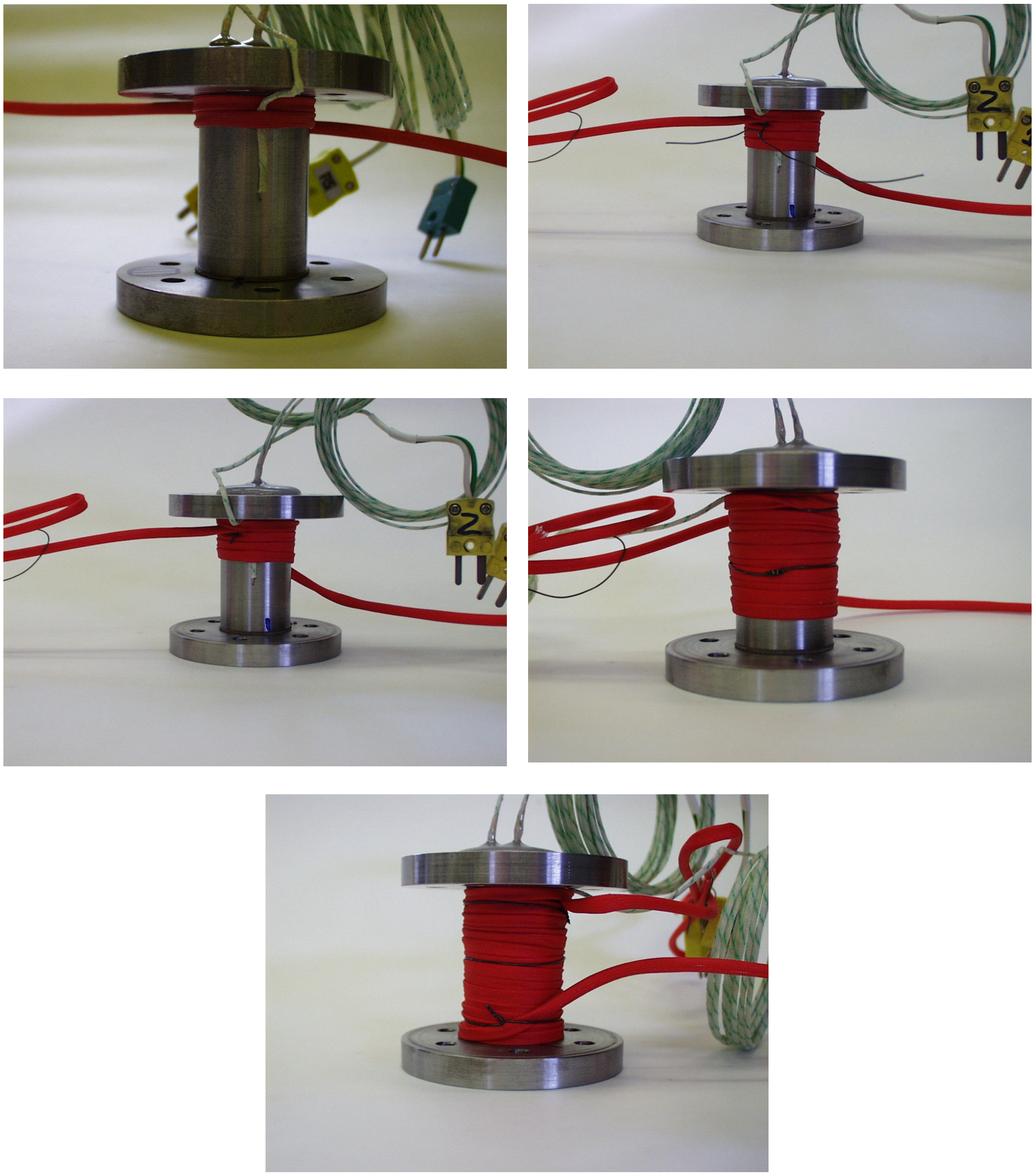

Figure 3.53 - Heating Wire System.

Figure 3.54 - Heating Insulation.

It was found advisable to protect the containment box from unnecessary damage by standing the vehicle on a thick plastic base, as shown.

The final operational configuration is shown in Figure 3.55.

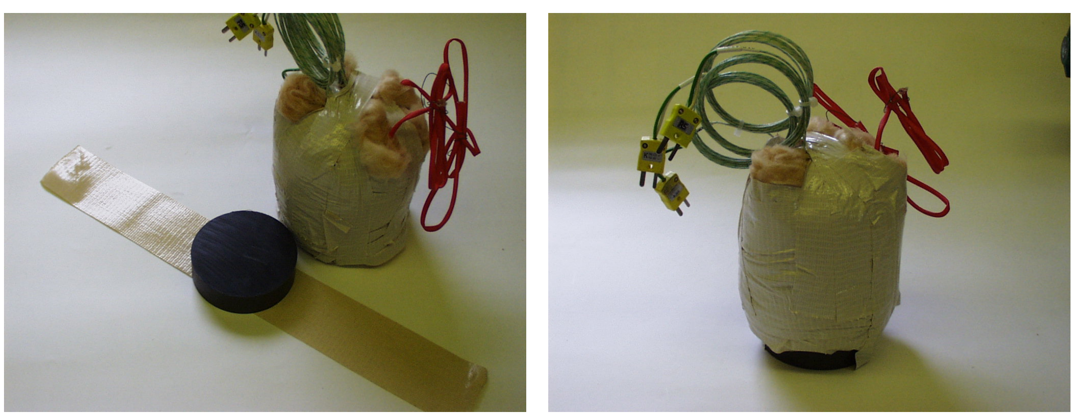

Figure 3.55 - Operational Configuration for Cook-Off Testing.

3.5. COOK-OFF TESTS

This section describes the preliminary tests performed to establish safe and efficient experimental procedures, and to optimise the power supply, heating rate control and data acquisition. It also includes experimental details and results of all the firing trials at fast and slow heating rate at small and medium scale.

Once a satisfactory process for carrying out the trials had been devised it was followed rigorously for all firings.

3.5.1. Preliminary Testing of the Cook-Off Test Equipment

Several blanks runs were performed in a small scale test vehicle in order to assess the:

- best location of the control thermocouple: budget restrictions eliminated the option of having the control thermocouple laser welded to the external surface of the test vehicle and, in order not to induce any weakness in the structure of the cook-off vehicle, the idea of having a control thermocouple welded into a orifice drilled on the outer surface of the test vehicle was immediately abandoned. Preliminary tests proved the best location for the thermocouple controlling the surface temperature, according to the pre-set heating rate, to be in the inside of the test vehicle as close as possible to the wall surface. The signal voltage from this thermocouple was used to drive the temperature controller, and was simultaneously fed to the data logger;

- power requirement to achieve the maximum heating rate for this experimental set up: it was established that the maximum heating rate that could be achieved consistently and reliably was about 360 K/h. To minimise problems that might be encountered in field trials under possibly widely different weather conditions, a lower rate of 240 K/h was selected for all subsequent Fast Cook-Off work. A lower heating rate of 3.3 K/h was selected and achieved without any problems and in a very reliable way. This heating rate, which is the recommended by STANAG 4382 (1996) for the Slow Cook-Off program, was used;

- <u>need of supplementary heat insulation of the test vehicle</u>: it was considered advisable to minimise the effect of varying ambient temperature by insulating the vehicle with a layer of Rock Wool;

- <u>need for protection of the bottom of the Fragmentation Containment Box</u>: due to the violence of response witnessed during some of the preliminary tests carried out with filled test vehicles, it was decided to apply a thick plastic disc to the bottom side of the Rock Wool for every test vehicle to minimise the damage caused to the Fragmentation Containment Box;

- <u>need to reinforce the sealing of the thermocouple and ferrule assembly</u>: during the only preliminary test in this series performed with a TNT filled small scale test vehicle one of the thermocouples was thrown out of the test vehicle. It was found that a reinforcement of the seal with an explosively compatible epoxy resin guaranteed that the thermocouples remained in place, and simultaneously ensured that the test vehicles is air tight during a trial.

A second series of preliminary tests was performed with filled small scale test vehicles to fine tune all the parameters of the temperature controller to ensure the most accurate and reproducible heating rate possible. The various settings of the temperature controller were adjusted to provide the smoothest curve, and once optimised, the settings were used for all the trials.

3.5.2. Fast Cook-Off

For the Fast Cook-Off trials a pre-selected thermal profile was input into the temperature controller: a first heating ramp from ambient temperature to 273 K at a rate of 300 K/h, then a dwelling period of 1 hour at 373 K, and finally a second heating ramp to 673 K at a rate of 240 K/h. This thermal profile was adjusted so that the complete experiment would require no more than 3 hours.

The results obtained for small and medium scale Cook-Off testing are presented in terms of time to Cook-Off and Cook-Off temperature for all the samples tested (see Table 3.VII).

The small scale Fast Cook-Off test performed with 25RDX/75TNT had to be repeated as it produced anomalous results, presenting a large temperature difference between the centre and the surface of the charge even when held at constant temperature (see Appendix III). An instrumentation problem was indicated. The new trial performed with the sample above mentioned produced the results indicated in Table 3.VII:

	SMALL SCALE			MEDIUM SCALE		
Sample	**t (s)**	**T_{TC1} (ºC)**	**T_{TC4} (ºC)**	**t (s)**	**T_{TC1} (ºC)**	**T_{TC4} (ºC)**
RDX	1582	191	203	1574	143	203.5
75RDX/25TNT	1189	166	182	999	117.5	161
60RDX/40TNT	1324	196.5	186.5	1212	144	177
50RDX/50TNT	1449	215.5	211.5	1149	219	220.5
40RDX/60TNT	1626	234.5	230	1423	----	220.5
25RDX/75TNT	1486	226.5	228.5	1558	229	223.5
TNT	1083	243	148	992	195.5	226.5

Table 3.VII - Experimental Results Obtained for Small and Medium Scale Fast Cook-Off Studies.

Typical examples of the Fast Cook-Off profiles obtained for small and medium scale for the same sample are presented in Figures 3.56 and 3.57, respectively. In Appendix III a compilation of the Fast Cook-Off profiles for all the samples trialled is presented.

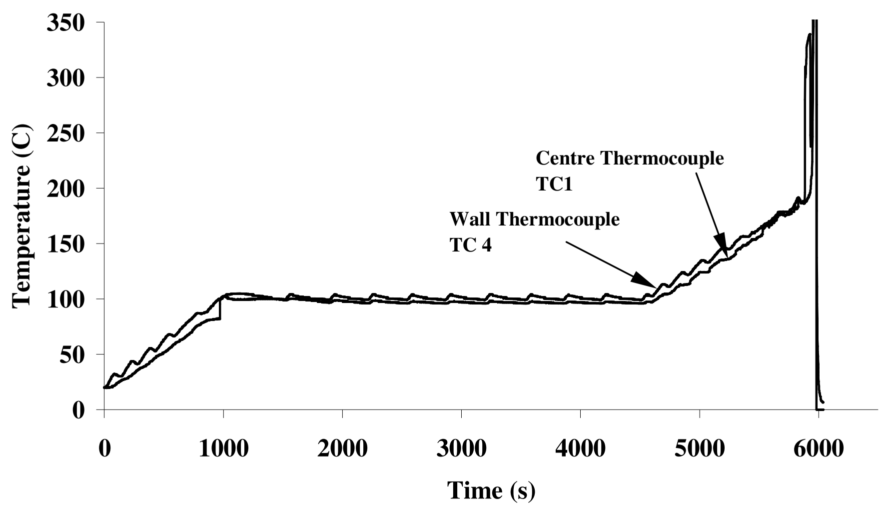

Figure 3.56 - Fast Cook-Off Profile of a Small Scale 60RDX/40TNT Charge.

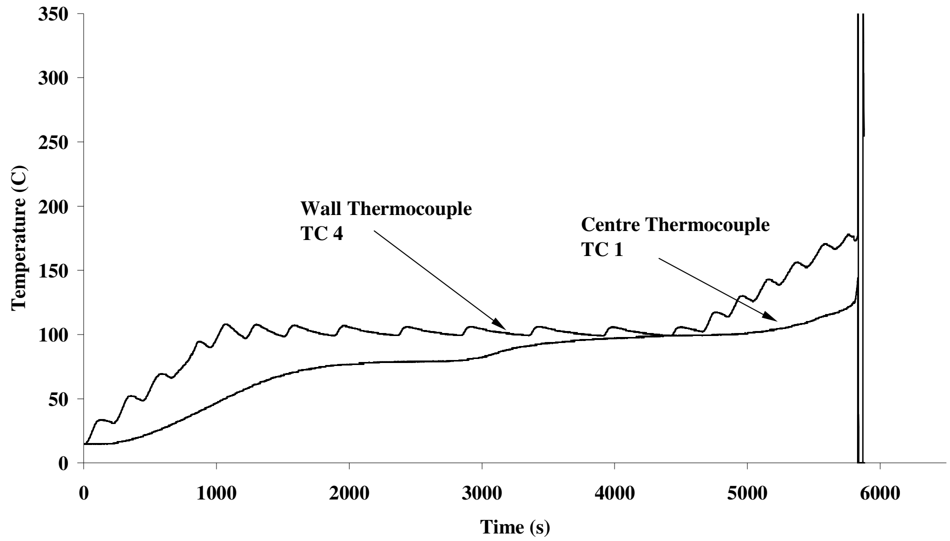

Figure 3.57 - Fast Cook-Off Profile of a Medium Scale 60RDX/40TNT Charge.

3.5.3. Slow Cook-Off

The Slow Cook-Off heating profile select comprised a first heating ramp from ambient temperature to 373 K at a rate of 300 K/h, then a dwelling period of 1 hour at 373 K followed, and finally a second heating ramp to 673 K at a rate of 3.3 K/h.

The results obtained for small and medium scale Cook-Off testing are presented below in terms of time to Cook-Off and Cook-Off temperature for all the samples tested (see Table 3.VIII).

	SMALL SCALE			MEDIUM SCALE		
Sample	**t (s)**	**T_{TC1} (ºC)**	**T_{TC4} (ºC)**	**t (s)**	**T_{TC1} (ºC)**	**T_{TC4} (ºC)**
RDX	82920	209	182	80370	209.5	189
75RDX/25TNT	84533	173	185.5	64813	194	171
60RDX/40TNT	90532	232.5	207	67040	189.5	188
50RDX/50TNT	73137	181.5	173	72256	190.5	193.5
40RDX/60TNT	74237	211.5	174	75309	170.5	169
25RDX/75TNT	80602	184.5	181.5	83105	182	239
TNT	121456	236.5	242.5	127595	228.5	225.5

Table 3.VIII - Experimental Results for Small and Medium Scale Slow Cook-Off Studies.

Typical examples of the Slow Cook-Off profiles obtained for small and medium scale for the same sample are presented in Figures 3.58 and 3.59, respectively. In Appendix III a compilation of the Slow Cook-Off profiles for all the samples trialled is presented.

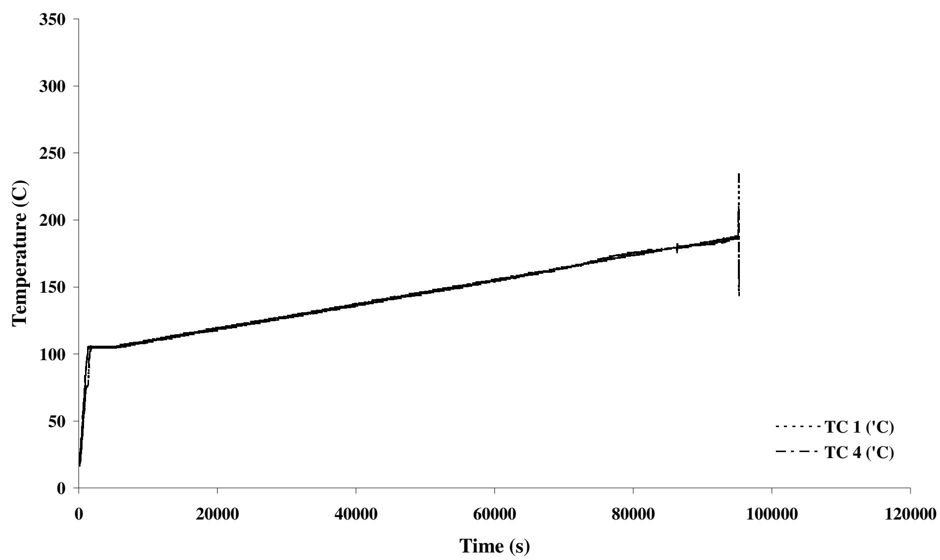

Figure 3.58 - Slow Cook-Off Profile of a Small Scale 60RDX/40TNT Charge.

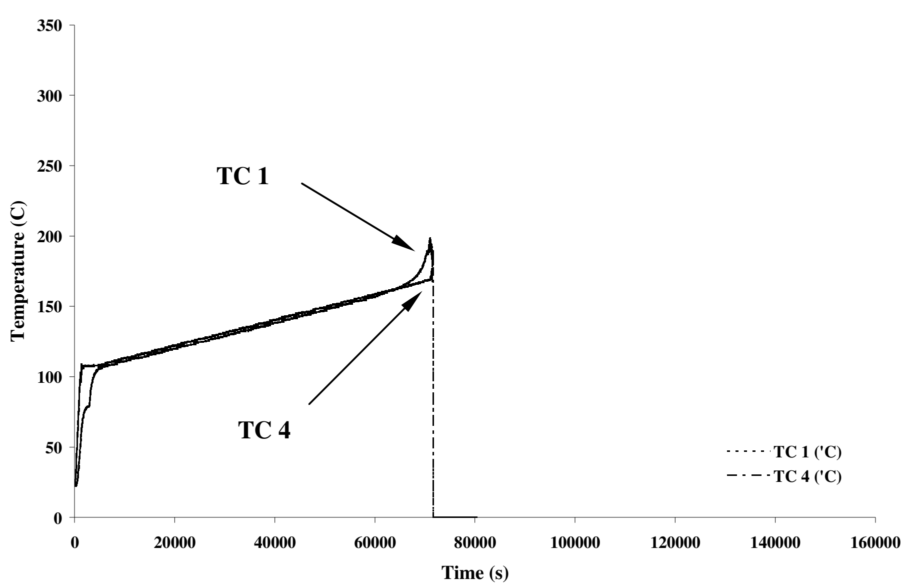

Figure 3.59 - Slow Cook-Off Profile of a Medium Scale 60RDX/40TNT Charge.

3.5.4. Effect of Heating Rate

The results presented above for Fast and Slow Cook-Off, for both scales, allow for the effect of heating rate on time and temperature to Cook-Off, at the same scale, to be indicated in Tables 3.IX and 3.X:

	FAST COOK-OFF			SLOW COOK-OFF		
Sample	**t (s)**	**T_{TC1} (ºC)**	**T_{TC4} (ºC)**	**t (s)**	**T_{TC1} (ºC)**	**T_{TC4} (ºC)**
RDX	1582	191	203	82920	209	182
75RDX/25TNT	1189	166	182	84533	173	185.5
60RDX/40TNT	1324	196.5	186.5	90532	232.5	207
50RDX/50TNT	1449	215.5	211.5	73137	181.5	173
40RDX/60TNT	1626	234.5	230	74237	211.5	174
25RDX/75TNT	1486	226.5	228.5	80602	184.5	181.5
TNT	1083	243	148	121456	236.5	242.5

Table 3.IX - Experimental Results Obtained for Small Scale Studies, at Different Heating Rates.

	FAST COOK-OFF			SLOW COOK-OFF		
Sample	**t (s)**	**T_{TC1} (ºC)**	**T_{TC4} (ºC)**	**t (s)**	**T_{TC1} (ºC)**	**T_{TC4} (ºC)**
RDX	1574	143	203.5	80370	209.5	189
75RDX/25TNT	999	117.5	161	64813	194	171
60RDX/40TNT	1212	144	177	67040	189.5	188
50RDX/50TNT	1149	219	220.5	72256	190.5	193.5
40RDX/60TNT	1423	----	220.5	75309	170.5	169
25RDX/75TNT	1558	229	223.5	83105	182	239
TNT	992	195.5	226.5	127595	228.5	225.5

Table 3.X - Experimental Results Obtained for Medium Scale Cook-Off Studies, at Different Heating Rates.

3.6. FRAGMENTATION ANALYSIS

The violence of event of the samples tested was qualitatively assessed on the basis of a visual examination of the types of fragments produced.

A standard to allow for this qualitative assessment was produced by means of a complete detonation of a 0.020 kg PE4 charge with a Nr. 8 Cap Electrical Detonator (see Fig. 3.60).

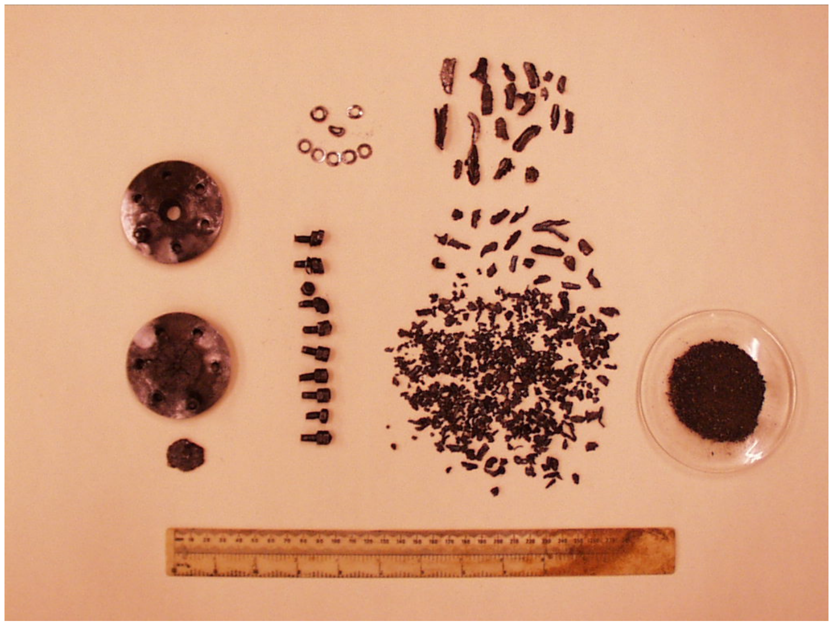

Figure 3.60 - Complete Detonation of a PE4 Charge.

The descriptors used are:

- Pressure Release - no fragments and only slight distortion of the vessel;
- Pressure Burst - no fragments, but disrupted and distorted vessel;
- Deflagration - large fragments;
- Detonation - small fragments.

The recovered pieces from the Cook-Off tests performed were arranged by type on A4 sheets of paper and photographed as a group. The photographs show separately:

- recovered thermocouples, whenever they were not still attached to the top end cap;
- heating wire, with the possibility of having the test vehicle's body attached;
- remains of bolts, nuts and bolts' washers;

- top and bottom end caps (with or without thermocouples, with or without remains of the protective disk of the operational configuration, an in very exceptional cases with remains of the vehicle engine gasket washers);

- in those cases where fragmentation of the test vehicle's body occurred 5th and 6th A4 paper sheets were used to spread the fragments divided by the following sieving ranges:

(i) $\geq$ 2500 µm;

(ii) between 1405 - 2500 µm;

(iii) < 1405 µm;

(iv) In very exceptional cases metallic dust is also included on an extra A4 paper sheet;

- in some cases the remains of the protective disk of the operational configuration and remains of Rock Wool are presented on separate A4 paper sheets too.

The results obtained for this study on the assessment of the violence of response are included in Tables 3.XI and 3.XII next.

	SMALL SCALE	MEDIUM SCALE
Sample	**Type of Response**	**Type of Response**
RDX	Detonation	Detonation
75RDX/25TNT	Deflagration	Deflagration
60RDX/40TNT	Deflagration	Deflagration
50RDX/50TNT	Pressure Burst	Deflagration
40RDX/60TNT	Deflagration	Deflagration
25RDX/75TNT	Deflagration	Deflagration
TNT	Pressure Release	Pressure Release
$TNT_{15\% void}$	Pressure Burst	Deflagration

Table 3.XI - Qualitative Assessment on the Violence of Response of the Explosives Tested on the Fast Cook-Off Program.

Sample	SMALL SCALE Type of Response	MEDIUM SCALE Type of Response
RDX	Deflagration	Detonation
75RDX/25TNT	Deflagration	Pressure Burst
60RDX/40TNT	Deflagration	Pressure Burst
50RDX/50TNT	Pressure Release	Pressure Burst
40RDX/60TNT	Pressure Release	Pressure Burst
25RDX/75TNT	Pressure Release	Pressure Burst
TNT	Pressure Release	Pressure Release

Table 3.XII - Qualitative Assessment on the Violence of Response of the Explosives Tested on the Slow Cook-Off Program.

In Appendix IV a compilation of the fragmentation profiles for all samples trialled is presented.

Chapter IV

RESULTS DISCUSSION

In this Chapter a discussion of the experimental results obtained in this study is offered. The aspects considered relevant for further development of the present Cook-Off test facility are also presented.

4.1. THERMAL ANALYSIS

The DSC results demonstrated that, in spite of repeated attempts to prevent leakage by annealing the aluminium crucibles at 673 K for 1 hour before crimping, sublimation of TNT was usually observed showing that the crucibles were not hermetically sealed. Therefore, the results obtained must not be taken as the exact values: these are nevertheless indicative, and the trends identified are valid.

At a heating rate of 10 K/minute pure TNT gives an exotherm above 573 K, and pure RDX gives an exotherm immediately after the melting endotherm at 477 K.

Our results are in agreement with the ones reported by Wilby (1967) who refers studies of decomposition of both single explosives TNT and RDX, and states experiments proved that both TNT and RDX are reasonably stable below the melting point of RDX (475.8 K).

In our experiments, mixtures of TNT with RDX show two exotherms at corresponding positions, but for slightly different temperatures from those obtained for the single explosives. As the proportion of RDX increases the size of the lower temperature exotherm increases and that of the higher temperature exotherm decreases until it is not observed for RDX content above 50%. This phenomenon could be due to the fact that RDX acts as a catalyst in the thermal degradation of TNT.

These observations are in agreement with the ones reported by Wilby (1967) on decomposition of RDX/TNT mixtures. According to this author, RDX in the presence of TNT decomposes below the melting point of RDX, and at a much faster rate than solid RDX at the same temperature. The author is of the opinion that such occurs as a result of RDX dissolving in TNT and decomposing in the liquid state, as RDX is appreciably soluble in TNT.

Furthermore the experiments of this author, when attempting to prove the mechanism of decomposition of RDX was a first order one, proved that for those cases where RDX was present in the mixture in a higher content than the one capable of dissolving in TNT, TNT was itself undergoing decomposition. RDX decomposition products are mainly gaseous whereas examination of the extensively decomposed residues was typical of black carbonaceous residues from TNT. TNT decomposition in the presence of RDX was much faster than would be obtained from TNT alone, suggesting that the simple kinetic model proposed is complicated by the RDX decomposition products catalysing the decomposition of TNT.

Further thermal analysis tests to confirm these observations are recommended to be pursued, as due to constraints of time and scope of study it was not possible to perform them.

4.2. COOK-OFF TESTS

4.2.1. Fast Cook-Off

Experiments performed with zero ullage whatever concerns the volume of explosive in the Cook-Off test vehicles show that at both scales, as the composition changes from pure TNT, through the RDX/TNT mixtures to pure RDX the time to Cook-Off rises to a maximum at 25% RDX (medium scale) or 40% RDX (small scale) then decreases to a minimum at 75% RDX (both scales) and then rises at pure RDX. The difference in times at different scales is similar for comparable samples.

There is a similar pattern for the Cook-Off temperatures. These trends are plotted in Figures 4.1 and 4.2.

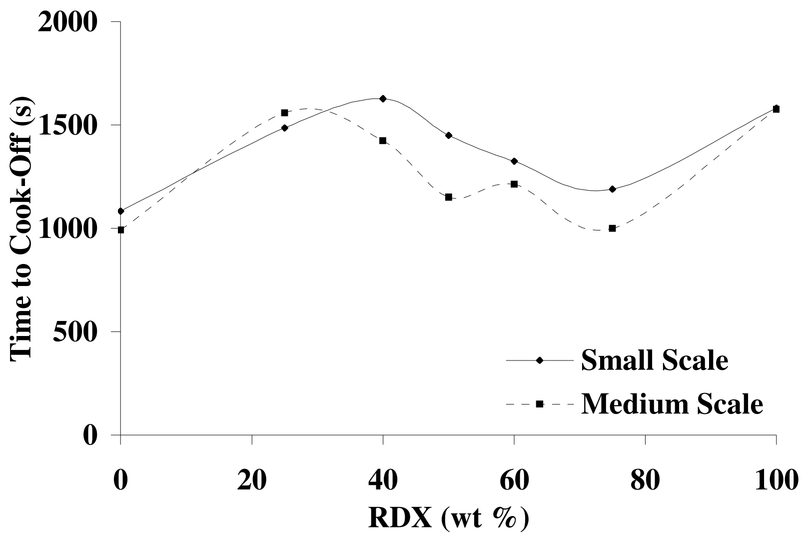

Figure 4.1 - Time to Cook-Off vs. RDX Content Profile for Small and Medium Scale Cook-Off Tests, with RDX/TNT Mixtures.

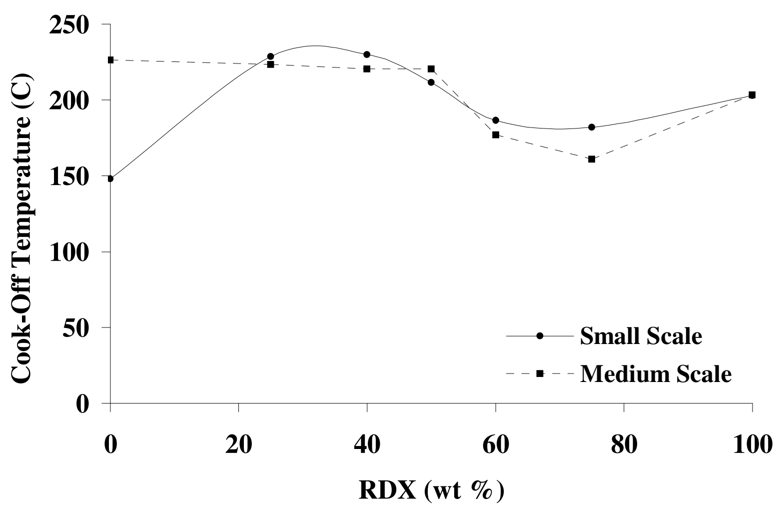

Figure 4.2 - Temperature at Cook-off vs. RDX Content Profile for Small and Medium Scale Cook-Off Tests, with RDX/TNT Mixtures.

The Fast Cook-Off tests performed with TNT present low values for time to Cook-Off and Cook-Off temperature on both scales. These initial tests were performed with 0% ullage. As TNT expands on melting, another series of experiments were performed with 15% of ullage. The results obtained for small and medium scale were, respectively (see Table 4.I):

TNT $_{15\%\ ullage}$	**T (s)**	**T_{TC1} (ºC)**	**T_{TC4} (ºC)**
Small Scale	2808	318	314.5
Medium Scale	2670	288.5	288.5

Table 4.I - Experimental Results Obtained for Small and Medium Scale Cook-Off Tests on a TNT Sample with 15% Ullage.

Integrating these results on the trends plotted previously on Figures 4.1 and 4.2, it is clear the significant changes induced in the observed trends:

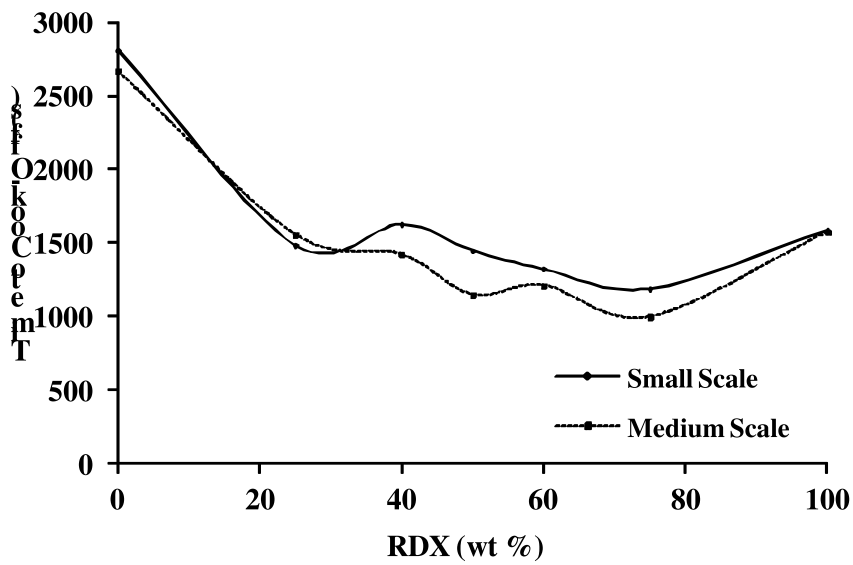

Figure 4.3 - Time to Cook-Off vs. RDX Content Profile for Small and Medium Scale Cook-Off Tests, with RDX/TNT Mixtures (TNT Samples With 15% Ullage).

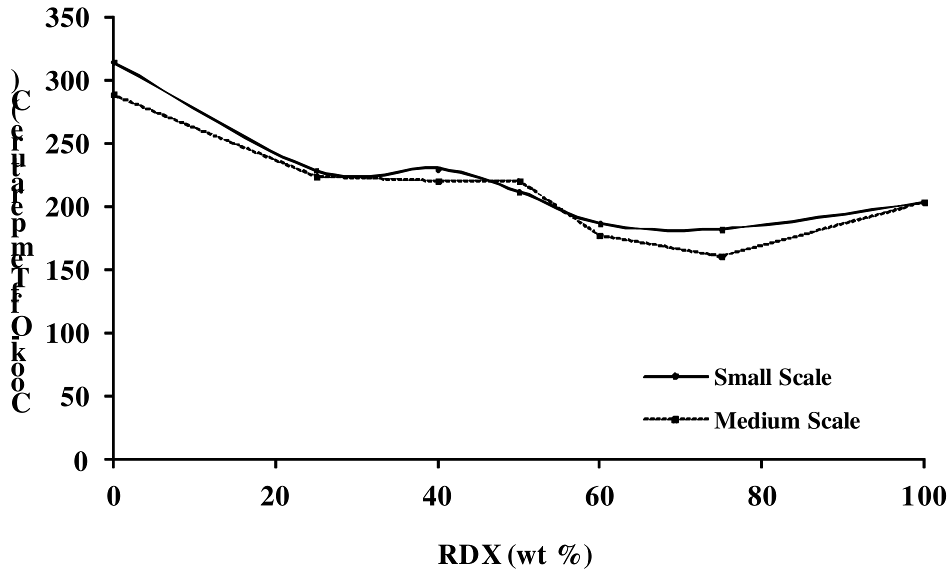

Figure 4.4 - Cook-Off Temperature vs. RDX Content Profile for Small and Medium Scale Cook-Off Tests, with RDX/TNT Mixtures (TNT Samples With 15% Ullage).

The mixture 50RDX/50TNT at medium scale appears to Cook-Off at an unexpectedly low time, but at an unexpectedly high measured temperature.

As only one Cook-Off test was performed per sample at both scales there is no statistical analysis possible of the trends presented for Fast Cook-Off.

4.2.2. Slow Cook-Off

All these experiments were conducted with no ullage.

The trends of time and temperature to Cook-Off vs. RDX content are plotted in Figure 4.5 and Figure 4.6. For time to Cook-Off, there is a general downward trend with increasing RDX content rising to pure RDX on the medium scale, but on the small scale there is an abrupt increase from 50% to 60% RDX. The temperatures are less clearly cut, but there appears to be a gentle downward trend with increasing RDX content.

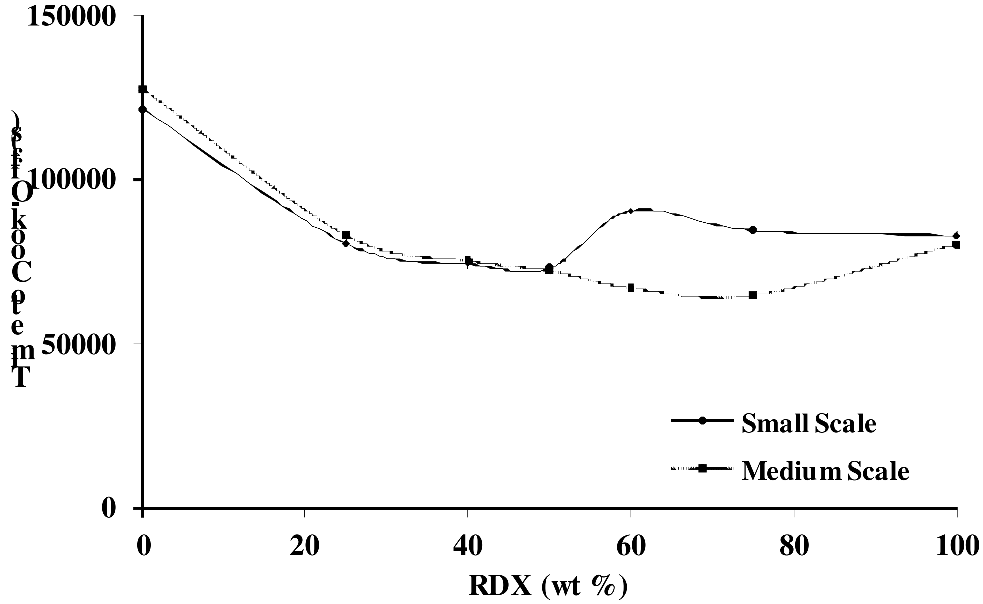

Figure 4.5 - Time to Cook-Off vs. RDX Content Profile for Small and Medium Scale Cook-Off Tests, with RDX/TNT Mixtures.

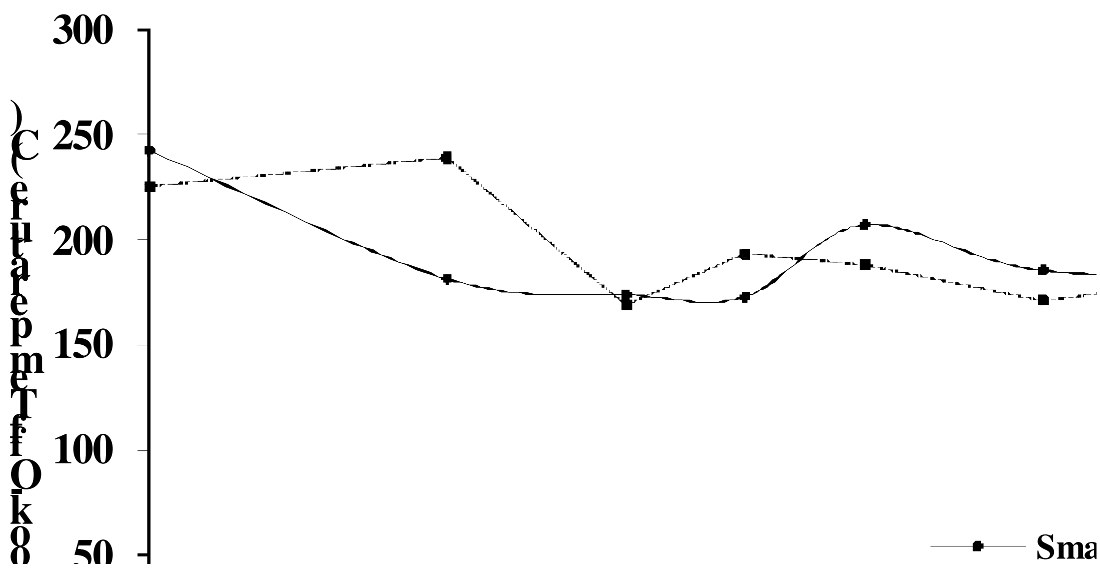

Figure 4.6 - Cook-Off Temperature vs. RDX Content Profile for Small and Medium Scale Cook-Off Tests, with RDX/TNT Mixtures.

Similarly to the fast cook-off firing program:

- the mixture 50RDX/50TNT at medium scale appears to Cook-Off at an unexpectedly low time, but at an unexpectedly high measured temperature;
- only one Cook-Off test was performed per sample at both scales and therefore it is not possible to perform a statistical analysis of the trends presented here for the Slow Cook-Off regime.

Effect of Heating Rate

The effect of heating rate on time and temperature to Cook-Off, at the same scale are presented for Fast and Slow Cook-Off, for both scales, in Tables 4.II (small scale) and 4.III (medium scale).

	FAST COOK-OFF			**SLOW COOK-OFF**		
Sample	**t (s)**	**T_{TC1} (ºC)**	**T_{TC4} (ºC)**	**t (s)**	**T_{TC1} (ºC)**	**T_{TC4} (ºC)**
RDX	1582	191	203	82920	209	182
75RDX/25TNT	1189	166	182	84533	173	185.5
60RDX/40TNT	1324	196.5	186.5	90532	232.5	207
50RDX/50TNT	1449	215.5	211.5	73137	181.5	173
40RDX/60TNT	1626	234.5	230	74237	211.5	174
25RDX/75TNT	1486	226.5	228.5	80602	184.5	181.5
TNT	1083	243	148	121456	236.5	242.5

Table 4.II - Experimental Results Obtained for Small Scale Studies, at Different Heating Rates.

	FAST COOK-OFF			**SLOW COOK-OFF**		
Sample	**t (s)**	**T_{TC1} (ºC)**	**T_{TC4} (ºC)**	**T (s)**	**T_{TC1} (ºC)**	**T_{TC4} (ºC)**
RDX	1574	143	203.5	80370	209.5	189
75RDX/25TNT	999	117.5	161	64813	194	171
60RDX/40TNT	1212	144	177	67040	189.5	188
50RDX/50TNT	1149	219	220.5	72256	190.5	193.5
40RDX/60TNT	1423	----	220.5	75309	170.5	169
25RDX/75TNT	1558	229	223.5	83105	182	239
TNT	992	195.5	226.5	127595	228.5	225.5

Table 4.III - Experimental Results Obtained for Medium Scale Cook-Off Studies, at Different Heating Rates.

These tables demonstrate that for both scales, for small and medium scales, as the heating rate increases there is a decrease in time to Cook-Off and in most cases, an increase in Cook-Off temperature.

In summary, we may state that the small and medium scale Fast Cook-Off results show a trend with respect to time to Cook-Off for the RDX/TNT mixtures: the higher the RDX content in the mixture the shorter the time to Cook-Off. With respect to the Cook-Off temperatures, there is similarly a decrease of these with the increase on RDX content in the RDX/TNT mixtures.

Concerning both trends on time to Cook-Off and Cook-Off temperature, the mixture 50RDX/50TNT for medium scale seems to be the one presenting an exceptional behaviour. No explanation for this apparent exception has been so far found.

For the pure explosives, although RDX presents similar values for both time and temperature of Cook-Off for both scale sizes, there is, however, a reduction in Cook-Off time on moving from small to medium scale Cook-Off test vehicles.

As for TNT, tests with 0% ullage showed pressure release for lower values of time to Cook-Off and Cook-Off temperature on both scales. Further testing with 15% ullage resulted in higher values for both time and temperature to Cook-Off on either scales as well as a higher violence of response.

The Slow Cook-Off results for the mixtures show that for medium scale Cook-Off the time to Cook-Off decreases linearly with increasing RDX content. At small scale, however, very similar results are obtained for 25%, 40% and 50% RDX, but there was a marked rise to 60% and 75%, for reasons presently unclear. The trends of time to Cook-Off vs. RDX content show results for pure TNT and for pure RDX very similar at both scales, the small scale result for TNT being slightly shorter, and for RDX slightly longer.

The variation of Cook-Off temperature is more complex. RDX gives similar values at both scales, that at small scale being lower than that at medium scale. TNT gives a lower value at medium scale than at small scale. The values for mixtures differ sometimes markedly, between the two scales. At medium scale the Cook-Off temperature for 25%, 50%, 60% and 75% RDX decrease in a linear fashion, while the result for 40% RDX is very low. At small scale the Cook-Off temperatures for 25%, 40% and 50% RDX decrease linearly, and rise at 60% RDX, and then fall at 75% RDX.

Concerning both trends for time to Cook-Off and Cook-Off temperature, the mixture 50RDX/50TNT for medium scale seems to be the one presenting an exceptional behaviour.

In either regime, Fast and Slow Cook-Off, any apparent anomalies in the results obtained in both scales induce the recommendation that further tests should be performed in order to allow for a statistical analysis of the Cook-Off behaviour of these explosive systems under these experimental conditions.

4.3. FRAGMENTATION ANALYSIS

The basic fragmentation analysis results reflect a qualitative assessment of the violence of response.

The Fast Cook-Off results reflect for small scale Cook-Off of RDX/TNT mixtures a trend of increase in violence of response with increasing RDX content in the mixtures, except for the 50RDX/50TNT and 75RDX/25TNT mixtures, for as yet unknown reasons.

For the medium scale, again the same trend is observable, although the 60RDX/40TNT mixture appears to behave somewhat less violently than its neighbours.

The Slow Cook-Off results indicate that at small scale there is no significant difference in the violence of response for low to moderate RDX content (25 - 50%). At medium scale a similar situation occurs for the mixtures with RDX content varying between 25% and 60%.

Concerning the effect of scale on the violence of response, for both Fast and Slow Cook-Off trials, one can observe that, in most cases, there is an increase of the violence of response with the increase in the dimensions of the test vehicles, the exceptions being the 60RDX/40TNT and 75RDX/25TNT mixtures of the Slow Cook-Off testing.

In either regime, Fast and Slow Cook-Off, any apparent anomalies in the results obtained in both scales induce the recommendation that further tests should be performed with a specially designed and constructed fully confined test vehicle in order to allow for a statistical analysis of the Cook-Off violence of response of these explosive systems under these experimental conditions (e.g. scales and heating rates).

Chapter V

EXPERIMENTAL MODELLING

This chapter describes some attempts to model the Cook-Off tests carried out in this study. The aspects considered relevant for the development of the present study are detailed.

5.1. THEORY OF MODELLING

Many authors have modelled the time to event, with varying success, in the various experimental configurations in which they were interested.

The problem is that of solving the heat equation for a reacting material. Heat transfer within the vessel is usually assumed to be conductive, and heat losses convective.

The basic Heat Conduction Equation (Fourier's Law) states that the rate, q_x, at which thermal energy flows across a surface of area, A, normal to a temperature gradient ΔT/Δx is:

$$q_x \propto A\frac{\Delta T}{\Delta x} \tag{5.1}$$

The constant of proportionality is the *thermal conductivity*, *k*, and in the limit:

$$q_x = -Ak\frac{dT}{dx} \tag{5.2}$$

and the heat flux (power per unit area) is:

$$q_x'' = -k\frac{dT}{dx} \qquad [5.3]$$

The heat flux is a vector quantity, and generalising:

$$q_x'' = -k\nabla T = -k\left(i\frac{\partial T}{\partial x} + i\frac{\partial T}{\partial y} + k\frac{\partial T}{\partial z}\right) \qquad [5.4]$$

where ∇ is the three-dimensional del operator, and $T(x,y,z)$ is the scalar temperature field.

The Heat Diffusion Equation may be derived as follows (Incroptera & de Witt, 1990): considering a temperature gradient within an elemental parallelepiped in a homogeneous medium. In Cartesian co-ordinates, the heat rates *into* the volume (see Fig. 5.1) are q_x, q_y, and q_z.

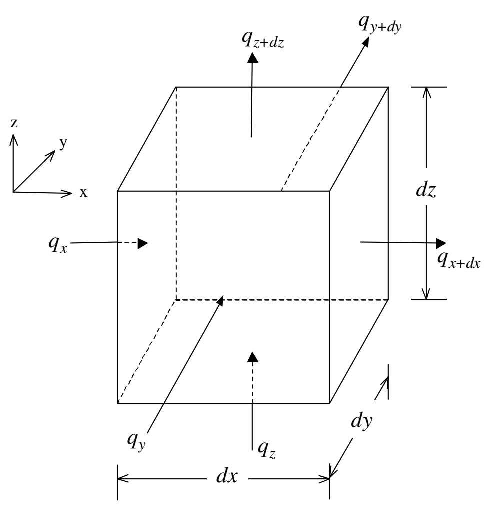

Figure 5.3 - Temperature Gradient Within an Elemental Parallelepiped in a Homogeneous Medium.

The conduction heat rates *out of* the volume may be approximated by the first terms of a Taylor series expansion:

$$q_{x+dx} = q_x + \frac{\partial q_x}{\partial x}dx; \quad q_{y+dy} = \frac{\partial q_y}{\partial y}dy; \quad q_{z+dz} = \frac{\partial q_z}{\partial z}dz \qquad [5.5]$$

If there is an energy source (in our case, due to a chemical reaction) *dq/dt* per unit volume, the total rate of energy generation is:

$$\frac{dE_g}{dt} = \frac{dq}{dt} dx dy dz \qquad [5.6]$$

If the temperature changes, the change in internal (stored) energy is:

$$\frac{dE_{st}}{dt} = \rho c_p \frac{dT}{dt} dx dy dz \qquad [5.7]$$

Then, by conservation of energy:

$$\frac{\partial E_{in}}{\partial t} - \frac{\partial E_{out}}{\partial t} + \frac{\partial E_g}{\partial t} = \frac{\partial E_{st}}{\partial t} \qquad [5.8]$$

$$q_x + q_y + q_z - q_{x+dx} - q_{y+dy} - q_{z+qz} + \frac{dq}{dt} dx\, dy\, dz = \rho c_p \frac{\partial T}{\partial t} dx\, dy\, dz \qquad [5.9]$$

From Fourier's Law:

$$q_x = -k\, dy\, dz \frac{\partial T}{\partial x}; \quad q_y = -k\, dx\, dz \frac{\partial T}{\partial y}; \quad q_z = -k\, dx\, dy \frac{\partial T}{\partial z} \qquad [5.10]$$

Hence, the Heat Diffusion Equation is obtained:

$$\frac{\partial}{\partial x}\left(k \frac{\partial T}{\partial x} \right) + \frac{\partial}{\partial y}\left(k \frac{\partial T}{\partial y} \right) + \frac{\partial}{\partial z}\left(k \frac{\partial T}{\partial z} \right) + \frac{dq}{dt} = \rho c_p \frac{\partial T}{\partial t} \qquad [5.11]$$

Our problem is better couched in cylindrical co-ordinates:

$$\frac{1}{r}\frac{\partial}{\partial r}\left(kr \frac{\partial T}{\partial r} \right) + \frac{1}{r^2}\frac{\partial}{\partial \varphi}\left(k \frac{\partial T}{\partial \varphi} \right) + \frac{\partial}{\partial z}\left(k \frac{\partial T}{\partial z} \right) + \frac{dq}{dt} = \rho c_p \frac{\partial T}{\partial t} \qquad [5.12]$$

This may be more conveniently expressed (in any co-ordinate system) as

$$k\nabla^2 T + \frac{dq}{dt} = \rho\, c_p\, \frac{\partial T}{\partial t} \qquad [5.13]$$

In our case, *dq*/*dt* results from a chemical reaction, or several reactions in competition or in sequence, which release or absorb heat.

It is usual to assume that each of the participating reactions has a rate constant described by the Arrhenius Equation:

$$k = Ae^{(-E_a / RT)} \qquad [5.14]$$

where *A* is the pre-exponential factor, E_a is the activation energy, *R* is the universal gas constant (8.314 J K^{-1} mol^{-1}) and *T* is the absolute temperature. *A* and E_a are assumed constant and independent of temperature.

If such a reaction liberates *q* J mol^{-1}, then the rate of heat production is:

$$\frac{dq}{dt} = qAe^{(-E_a / RT)} \qquad [5.15]$$

So, we seek to solve:

$$k\nabla^2 T + qAe^{(-E_a / RT)} = \rho\, c_p\, \frac{\partial T}{\partial t} \qquad [5.16]$$

It is generally recognised that a single chemical reaction does not give agreement with experiment. The following description is taken from McGuire & Tarver (1981):

Decomposition of TNT

According to Guidry & Davies (1978), quoted by McGuire & Tarver (1981), the decomposition reaction scheme suggested for TNT is essentially autocatalytic and takes place in three stages:

A → B (1)

A + B → C (2)

B + B → C (3)

In stage (1) a reactive immediate (B) is formed, which subsequently reacts with TNT molecules (A) during stage (2) to produce final gaseous products (C).

If q_j is the heat of reaction, A_j and E_{aj} the Arrhenius parameters of reaction j and N_i the mol fraction of constituent i, we may write the heat equation as:

$$k\nabla^2 T + N_A q_1 A_1 e^{(-E_1/RT)} + N_A N_B q_2 A_2 e^{(-E_2/RT)} + N_B^2 q_3 A_3 e^{(-E_3/RT)} = \rho\, c_p \frac{\partial T}{\partial t} \qquad [5.17]$$

As in our experiments we pre-condition the sample to 373 K we may ignore the melting of TNT.

Decomposition of RDX

The decomposition mechanism for RDX involves three reactions (McGuire & Tarver, 1981):

A → B (1)

B → 2C (2)

2C → D (3)

The first reaction is an endothermic reaction, involving the breaking of the C-N bonds in the ring forming $H_2C{=}N{-}NO_2$ and other ring fragments. This reaction seems to be the slowest of the decomposition steps. Reaction (2) is the slightly exothermic rearrangement of $H_2C{=}N{-}NO_2$ into either CH_2O and N_2O or HCN and HNO_2, which leads to $\cdot NO_2$ radicals. The final reaction is a very exothermic gas phase decomposition of CH_2O + N_2O (and/or HCN + HNO_2) into the stable gaseous products H_2O, N_2, CO, CO_2, etc..

Therefore, the Heat Equation is written as:

$$k\nabla^2 T + N_A q_1 A_1 e^{(-E_1/RT)} + N_B q_2 A_2 e^{(-E_2/RT)} + N_C^2 q_3 A_3 e^{(-E_3/RT)} = \rho\, c_p \frac{\partial T}{\partial t} \qquad [5.18]$$

As RDX melts at 477 K, a term for its melting during the self-heating following the constant temperature soak should be included. The modified equation, consequently, becomes:

$$k\nabla^2 T + N_1 q_1 A_1 e^{(-E_1/RT)} + N_2 q_2 A_2 e^{(-E_2/RT)} + N_3^2 q_3 A_3 e^{(-E_3/RT)} = \rho c_p \frac{\partial T}{\partial t} + \Delta H_{fus} \qquad [5.19]$$

5.2. Solution of the Equations

The equations were solved using the commercial software FlexPDE©, a scripted finite element model builder and numerical solver[5] which allows the problem to be described relatively simply in terms of geometry, materials properties, and the differential equations defining the heat flow and the reaction kinetics[6]. The program allows the geometry of the system to be described in the most applicable co-ordinate system, the relevant thermal properties of the materials to be assigned to the various domains, and the heat flow equation to be written in a conventional form. The geometry of the experiment has a vertical axis and a horizontal plane of symmetry. This can clearly be dealt with as a two dimensional problem without loss of generality.

In the absence of better data, the thermal transport values were considered constant, and convection within the vessel was ignored. The fusion of RDX was handled by the computational device of using a heat capacity equal to the heat of fusion over a narrow temperature range around the melting point of RDX (477 K). The heat capacity of molten RDX was assumed to be that of the solid, an approximation perhaps justified by the rapid decomposition of molten RDX which leaves only a small concentration present in the system at any one time.

The Arrhenius parameters and heats of reaction (McGuire & Tarver, 1981) used here are shown in Table 5.I. Unfortunately, and rather surprisingly, values for RDX/TNT have not been found in the literature. It is likely that in the mixture the first species to decompose is the RDX in solution (solubility approximately 4.1% at 354 K), and no kinetic parameters have been found in the literature.

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[5] FlexPD Version 2.2 (2-dimensional) PDE Solutions Inc., P.O. Box 4217, Antioch, CA 94531-4217.

5.3. SETTING UP THE MODEL

The hardware is assumed to have cylindrical symmetry and to consist of a right cylindrical steel tube of uniform wall thickness capped at each end with a steel disc of uniform thickness. The capped cylinder is filled completely with explosive of uniform density and properties. The temperature of the outer wall of the tube is constrained to rise at a constant rate from the initial temperature. Heat is lost from the end caps by convection (radiation was ignored at the relatively low temperature of the experiment), and heat is generated by the temperature dependent decomposition of the explosive.

The problem is set up within the code in the following manner, which will be made clear by reference to the codes for TNT and for RDX in Section 5.4 below.

COORDINATES The system is clearly cylindrical, and defining the relevant co-ordinate system allows the geometry to be simply described in terms of radius (R) and length (Z).

SELECT The colours are set for red (hot) and black/blue (cold). The error limit is the error within which the calculation is performed within a cell, and is set at the default value.

VARIABLES All variables are defined. The quantities aa, bb, and cc, are the concentrations of the three species considered in the decomposition scheme assumed here.

DEFINITIONS The constants used in the calculations are defined here. (Note that in the RDX code the heat of fusion of the explosive is allowed for by varying the heat capacity for the explosive from the value for the solid {assumed to be identical to that of the liquid} to that of the heat of fusion in a narrow range around the melting point).

INITIAL VALUE The initial (soak) temperature of the experiment is Ts, and the only species present is RDX (or TNT), therefore aa = 1, bb = cc = 0.

[6] The modelling work presented here is based on a software code written by Dr Nigel Davies - Senior Lecture of Royal Military College of Science/Cranfield University.

EQUATIONS The four variables require four equations. The first is the heat equation (5.17 above), the next three describe the three chemical reactions in the assumed kinetics scheme.

BOUNDARIES The geometry is defined by the two dimensional Cartesian co-ordinates of the edges of the boundary in sequence. Region 1 defines the outer dimensions of the case, Region 2 defines the explosive. Because of the symmetry of the experimental system, only a portion of the region needs to be defined and used in the calculation. In two dimensions this is the area in the plane of the axis of symmetry defined by the centre of the charge, a position on the axis (Region 1 - the centre of the outside of the lower end cap, Region 2 - the centre of the lower surface of the charge), the outside radius of the lower surface (end cap and charge respectively), and the radius from the centre of the charge (to the outer surface of the case, or of the charge respectively). The materials properties are defined for each region. Immediately before the geometrical definition the boundary conditions are specified. The outer surface of the case is constrained to rise in temperature at a specified rate; the end caps lose heat convectively, and the axis of the system, and the central plane perpendicular to it are adiabatic.

TIME The duration (in simulated time) of the calculation is defined.

PLOTS Various graphical outputs can be specified, at the cost of increased computation time.

The values used for the various quantities are given in Tables 5.II and 5.III below. The heating rates were 3.3 K/h (9.166 x 10^{-4} K s^{-1}) for Slow Cook-Off, and 240 K/h (6.667 x 10^{-2} K s^{-1}) for Fast Cook-Off.

Parameter	RDX	TNT	
q_1	-4.182E+05	-1.255E+05	J kg^{-1}
A_1	5.760E+19	1.586E+15	s^{-1}
E_{a1}	1.970E+05	1.840E+05	J mol^{-1}
q_2	1.255E+06	3.764E+06	J kg^{-1}
A_2	4.740E+17	1.957E+11	s^{-1}
E_{a2}	1.844E+05	1.443E+05	J mol^{-1}
q_3	5.018E+06	3.889E+06	J kg^{-1}
A_3	1.586E+15	2.391E+11	s^{-1}
E_{a3}	1.426E+05	1.401E+05	J mol^{-1}

Table 5.IV - Kinetic Parameters for RDX and TNT.

Quantity		Small Scale	Medium Scale
Case Length	(m)	0.0408	0.0956
Case Radius	(m)	0.0120	0.0245
End Cap Protrusion	(m)	0.0060	0.0060
Flange Thickness	(m)	0.0080	0.0080
Cap Diameter	(m)	0.0640	0.1000
Explosive Charge Length	(m)	0.0288	0.0866
Explosive Charge Radius	(m)	0.0105	0.0215
Case Wall Thickness	(m)	0.0025	0.0030

Table 5.II - Dimensions of Apparatus and Properties.

Quantity		Steel	TNT	RDX
Thermal Conductivity	(W m^{-1} K^{-1})	40	0.24	0.24
Specific Heat	(J kg^{-1} K^{-1})	500	1400	1400
Density - Crystal	(kg m^{-3})	6700	1700	1700
Density – Bulk	(kg m^{-3})			1000
Heat of Fusion	(J kg^{-1})			1.606×10^5
Melting Point	(K)			477
Heat Transfer Coefficient (Steel - Air)	(W m^{-2} K^{-1})	0 - 5		

Table 5.III - Properties of Materials.

5.4. Results

General Observations

The first phenomenon of interest is the position within the charge at which the thermal changes occur. It is commonly accepted that the thermal runaway occurs near the centre of the charge at slow heating rates, and at the surface at high heating rates.

The effect of heating rate (TNT in the medium scale experiment) on the position of the maximum temperature is shown in Figure 5.2 (first appearance outside the wall) and Figure 5.3 (explosion). The point (0, 0) is at the centre of the charge, and (21.5, -41.8) is at the bottom edge of the charge.

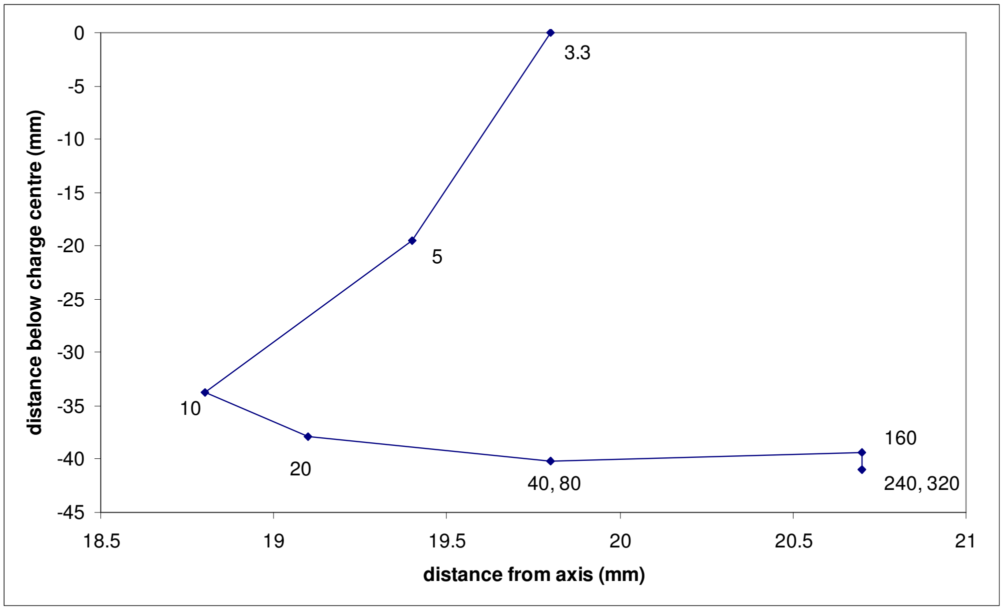


Figure 5.2 - Calculated Position of Emergence of Hot Spot at Different Heating Rates (e.g. Values Indicated Near the Data Points in the Graphic, in K/h).

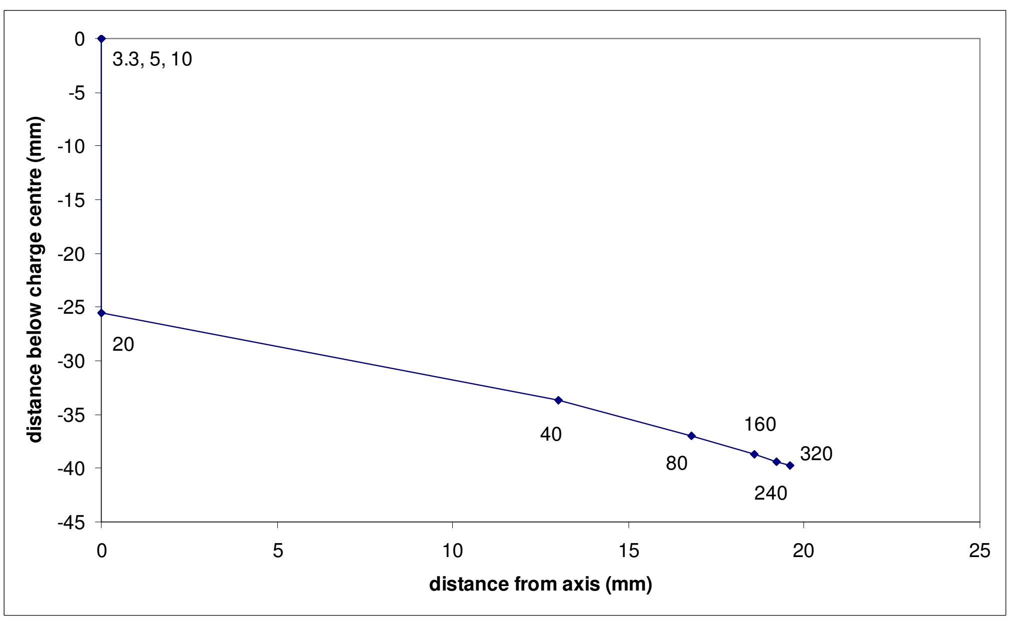


Figure 5.3 - Calculated Position of Cook-Off at Different Heating Rates (e.g. Values Indicated Near the Data Points in the Graphic, in K/h).

At low heating rate, self-heating first becomes important near the wall half way along the charge. As the heating rate is increased, the position moves slightly away from the wall and towards the end of the charge, and at still higher rates it moves back towards the wall. Subsequent migration of the hot zone results in explosion at the centre of the charge (3.3, 5, 10 K s^{-1}), on the axis but not at the centre (20 K s^{-1}), and at higher rates increasingly towards the corner of the charge.

Figure 5.4 shows a typical migration. The isotherms in the explosive and case are calculated for TNT in the medium scale hardware heated at 10 K s^{-1} for times from 3.83 x 10^4 s (when the maximum temperature in the system was moving from the heated wall into the explosive) to 4.040 x 10^4 s shortly before explosion occurred. The pictures show the bottom right hand quadrant of the charge and case (centre of the charge is at the top left).

These observations indicate the importance of conduction of heat from the wall along the end cap.

Heat loss from the end of the cap was investigated briefly for the same system by varying the heat transfer coefficient from 0 (perfectly insulated) to 5 (considerable cooling). As shown in Table 5.IV the time to explosion was not greatly affected, the time to appearance of self-heating was more affected, and the position of first appearance of a hot spot varied from a point on the end cap to a point on the central radius of the charge.

H	**Time to Self-Heating**	**Position of Self-Heating**		**Time to Explosion**
	(s)	X (mm)	Y (mm)	(s)
0	38.200	19.8	-40.2	41.120
1	38.500	18.8	-33.8	41.130
5	38.600	19.8	0	41.150

Table 5.IV - Effect of End Heat Loss on Cook-Off.

The effect of the heating rate on the time to event was investigated for TNT and RDX at small and medium scales. Two geometries were investigated in which the end caps either had a flange of the actual size, or had no flange. The intention was to ascertain whether the slightly different distribution of temperature would affect the results.

The results are given in Table 5.V (TNT, medium scale), Table 5.VI (TNT, small scale), Table 5.VII (RDX, medium scale), Table 5.VIII (RDX, small scale) and the comparison between calculation and experimental measurement is given in Table 5.IX (TNT) and Table 5.X (RDX).

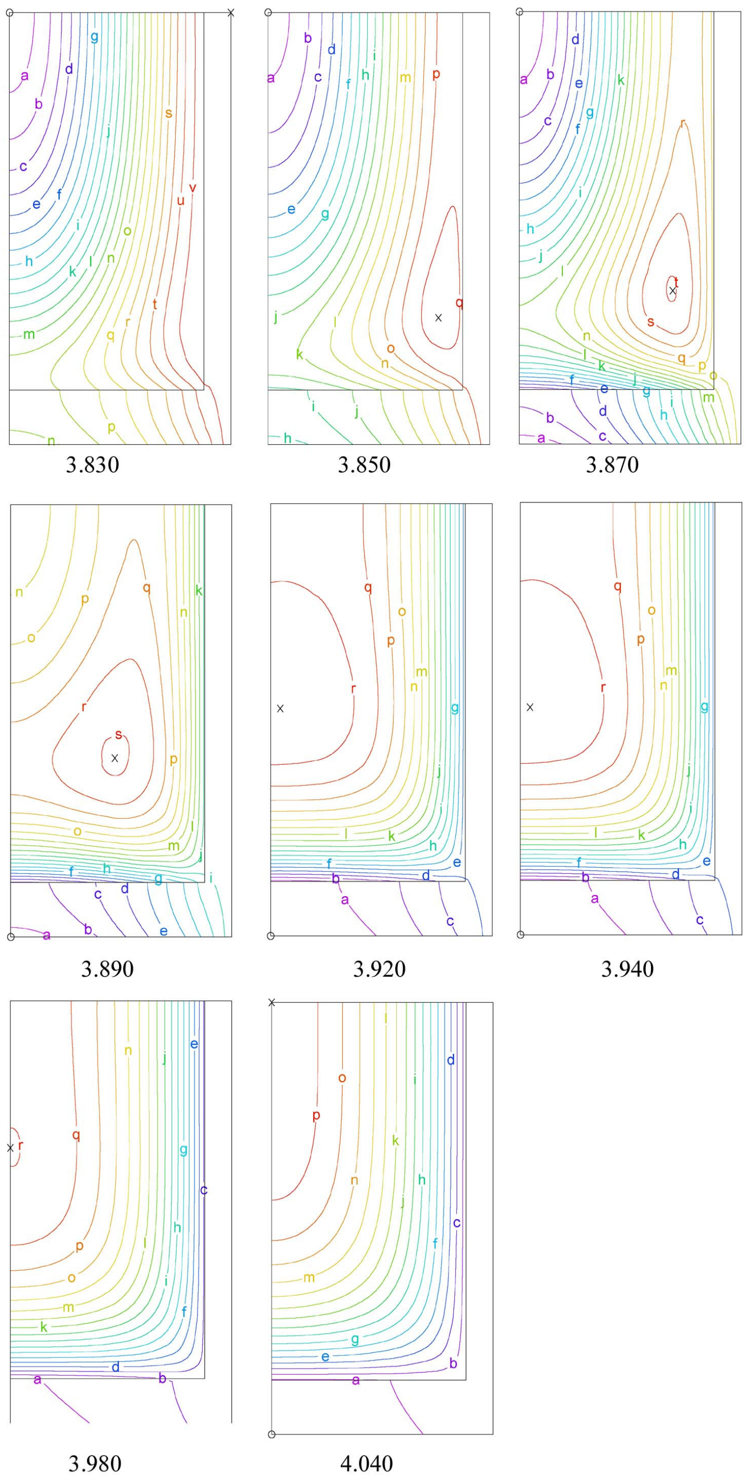


Figure 5.4 - Isotherms in TNT, Medium Scale Heated at 10 K/h (times/10^4 s).

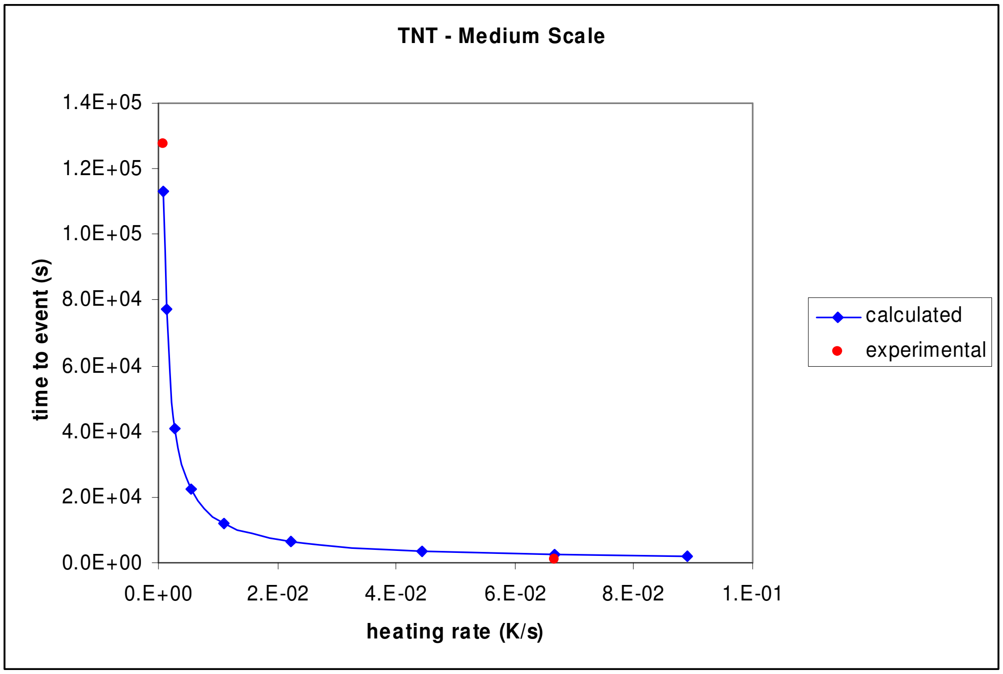


Figure 5.5 - Time to Event - TNT, Medium Scale.

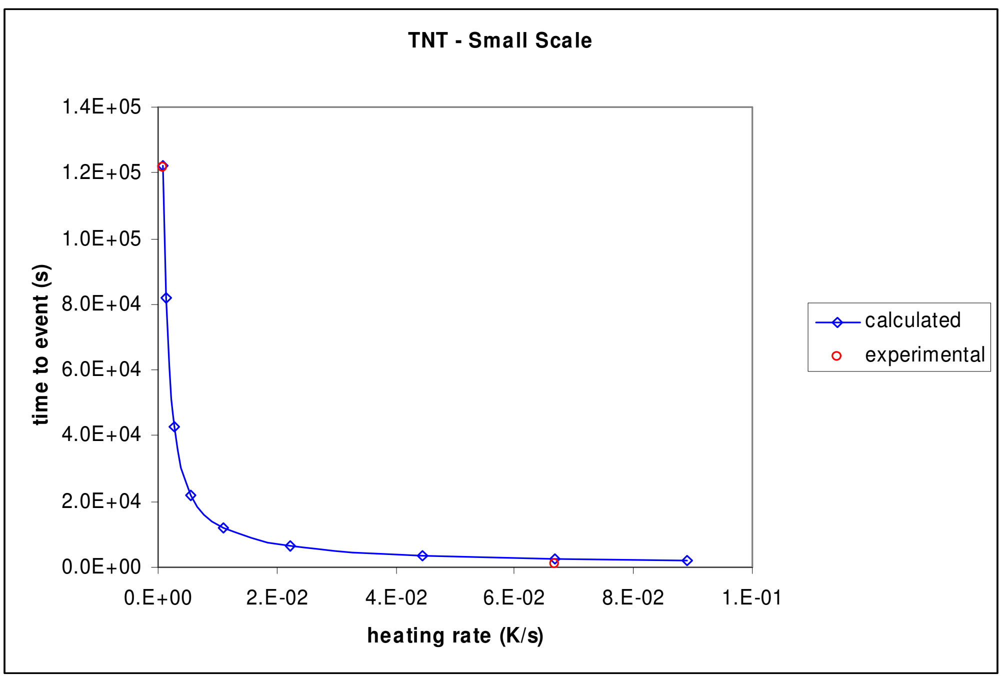


Figure 5.6 - Time to Event - TNT, Small Scale.

The modelling suggests that for TNT there should be very little difference between the two scales. The model is in reasonable agreement with experiment for Slow Cook-Off, but overestimates the time for Fast Cook-Off by a factor of two.

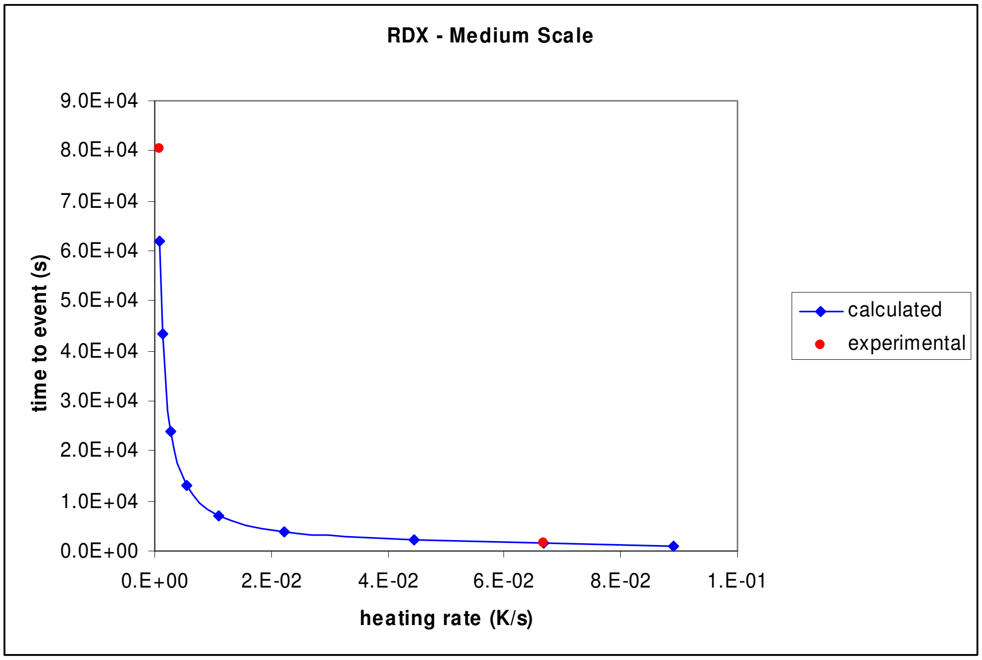


Figure 5.7 - Time to Event - RDX, Medium Scale.

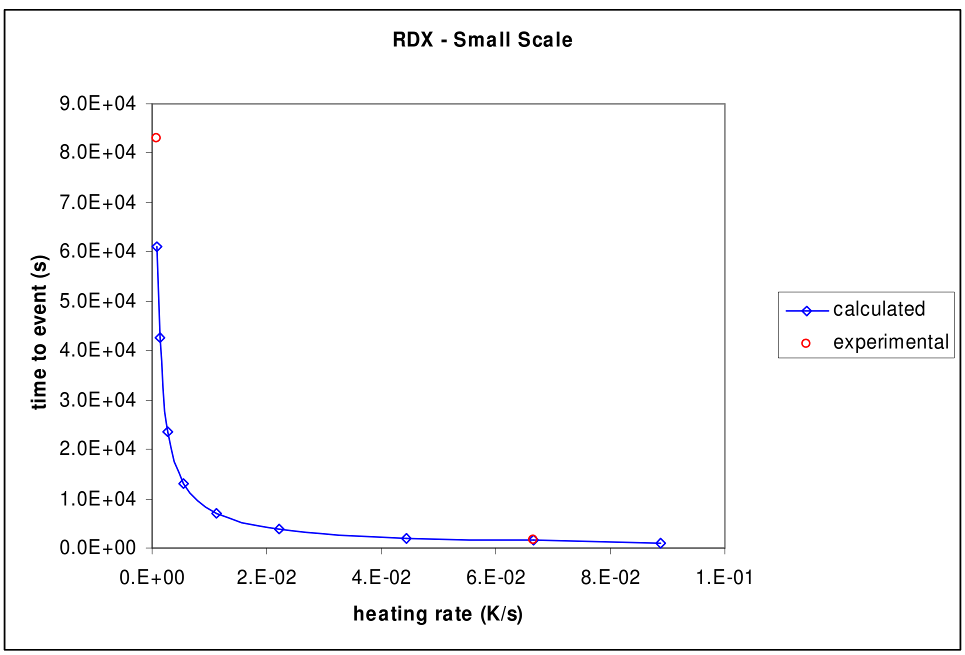


Figure 5.8 - Time to Event - RDX, Small Scale.

Again the modelling suggests that for RDX there should be very little difference between the two scales. Here, the model is in reasonable agreement with experiment for Fast Cook-Off, but underestimates the time for Fast Cook-Off by a factor of about 0.75.

Heating Rate		**First Hot Spot**					**Runaway**				
		Time		**Position**		**Wall Temp**	**Time**		**Position**		**Wall Temp**
				X	**Y**				**X**	**Y**	
(°/h)	(K s^{-1})	(s)	(h)	(mm)	(mm)	(K)	(s)	(h)	(mm)	(mm)	(K)
3.3	9.17E-04	102000	28.33	18.0	0	467	113000	31.39	0	0	479
5	1.39E-03	70800	19.72	16.9	-2.6	472	77300	21.48	0	0	480
10	2.78E-03	39000	10.83	13.0	-26.7	481	41000	11.41	0	0	487
20	5.56E-03	21000	5.83	18.6	-35.2	490	22300	6.15	0	-25.5	496
40	1.11E-02	11300	3.14	20.3	-36.8	498	12000	3.33	13.1	-33.5	506
80	2.22E-02	6100	1.69	19.9	-40.0	509	6440	1.79	16.8	-36.9	516
160	4.44E-02	3300	0.92	20.7	-39.1	520	3450	0.96	18.6	-38.7	526
240	6.67E-02	2300	0.64	20.7	-40.0	527	2390	0.66	19.3	-39.3	532
320	8.89E-02	1800	0.50	20.3	-40.5	533	1840	0.51	19.6	-39.7	537

Table 5.V - Calculated Cook-Off Times for TNT, Medium Scale.

Heating Rate		**First Hot Spot**					**Runaway**				
		Time		**Position**		**Wall Temp**	**Time**		**Position**		**Wall Temp**
				X	**Y**				**X**	**Y**	
(°/h)	(K s^{-1})	(s)	(h)	(mm)	(mm)	(K)	(s)	(h)	(mm)	(mm)	(K)
3.3	9.17E-04	102000	28.33	0	0	466	122000	33.92	0	0	485
5	1.39E-03	71000	19.72	0	0	472	82100	22.82	0	0	488
10	2.78E-03	38000	10.56	0	0	479	42700	11.86	0	0	490
20	5.56E-03	21000	5.83	0	0	489	22000	6.11	0	0	495
40	1.11E-02	11100	3.08	8.7	-9.4	496	11800	3.28	0	0	504
80	2.22E-02	6000	1.67	9.1	-10.9	504	6310	1.75	0	-4.0	514
160	4.44E-02	3210	0.89	9.8	-12.3	516	3390	0.94	5.9	-10.0	524
240	6.67E-02	2240	0.62	9.6	-13.5	522	2360	0.66	7.4	-11.2	530
320	8.89E-02	1730	0.48	9.6	-13.5	527	1820	0.51	8.1	-11.8	535

Table 5.VI - Calculated Cook-Off Times for TNT, Small Scale.

Heading Rate		First Hot Spot					Runaway				
		Time		Position		Wall Temp	Time		Position		Wall Temp
				X	Y				X	Y	
(°/h)	($K\ s^{-1}$)	(s)	(h)	(mm)	(mm)	(K)	(s)	(h)	(mm)	(mm)	(K)
3.3	9.17E-04	58700	16.31	20.3	-37.9	427	61811	17.17	31.1	-33.5	430
5	1.39E-03	41260	11.46	20.7	-39.1	430	43479	12.08	14.6	-36.3	432
10	2.78E-03	22800	6.33	20.7	-40.9	436	23970	6.66	17.2	-37.7	440
20	5.56E-03	12510	3.48	20.7	-40.9	442	13109	3.64	19.0	-39.0	446
40	1.11E-02	6820	1.74	21.1	-41.4	449	7125	1.98	19.8	-39.9	452
80	2.22E-02	3710	1.03	21.1	-41.4	455	3855	1.07	20.3	-40.7	459
160	4.44E-02	2010	0.56	21.3	-41.6	462	2077	0.58	20.6	-41.2	465
240	6.67E-02	1400	0.39	21.3	-41.6	466	1441	0.40	20.9	-40.9	469
320	8.89E-02	1090	0.30	21.3	-41.6	470	1100	0.31	21.4	-41.7	472

Table 5.VII - Calculated Cook-Off Times for RDX, Medium Scale.

Heading Rate		First Hot Spot					Runaway				
		Time		Position		Wall Temp	Time		Position		Wall Temp
				X	Y				X	Y	
(°/h)	($K\ s^{-1}$)	(s)	(h)	(mm)	(mm)	(K)	(s)	(h)	(mm)	(mm)	(K)
3.3	9.17E-04	57860	16.09	9.6	-9.8	426	61049	18.62	0.2	0	429
5	1.39E-03	40740	11.32	9.8	-11.8	430	42686	11.86	1.0	-0.7	432
10	2.78E-03	22580	6.27	9.8	-12.3	436	23612	6.56	2.9	-9.4	439
20	5.56E-03	12400	3.44	10.0	-13.9	442	12992	3.61	7.1	-10.8	445
40	1.11E-02	6770	1.88	10.0	-13.9	448	7080	1.97	9.0	-12.7	452
80	2.22E-02	3690	1.03	10.0	-13.9	455	3839	1.07	9.3	-13.1	458
160	4.44E-02	1990	0.55	10.3	-14.2	462	2039	0.57	9.2	-13.7	465
240	6.67E-02	1390	0.39	10.3	-14.2	466	1436	0.40	9.9	-13.6	469
320	8.89E-02	1080	0.30	10.3	-14.2	469	1108	0.31	10.0	-30.9	472

Table 5.VIII - Calculated Cook-Off Times for RDX, Small Scale.

			Small	**Medium**
Slow	3.3 K/h	experimental	121.456	127.595
		calculated	122.000	113.000
Fast	240 K/h	experimental	1083	992
		calculated	1820	1840

Table 5.IX - Experimental and Calculated Times (TNT).

			Small	Medium
Slow	3.3 K/h	experimental	82.920	80.370
		calculated	61.049	61.811
Fast	240 K/h	experimental	1582	1574
		calculated	1432	1441

Table 5.X - Experimental and Calculated Times (RDX).

5.5. Comments on the Model

No model can be better than the quality of the data it uses. This is a challenge in this model too. It is generally accepted that no single chemical equation for the decomposition of TNT or RDX can describe the observed phenomena, and three chemical equations seem necessary to give a reasonable result. However, the model derived here shows that these chemical equations do not describe the phenomena over the range of heating rates examined experimentally. For TNT reasonable agreement is obtained at slow heating rate, but the calculated time to Fast Cook-Off is double than that found experimentally. For RDX fair agreement is obtained at fast heating rate, but the calculated time to Slow Cook-Off is about 70% of that found experimentally.

The likely errors are predominantly:

Uncertainty in the kinetics. The literature contains different values for the Arrhenius constants for the same and different decomposition reactions determined by various experimental methods. Which values best describe the actual conditions can be ascertained only by trial and error. It may be that no single set of chemical reactions adequately describes the Cook-Off phenomenon over even the limited rage of heating rates and geometries investigated here.

Uncertainty in the thermal transport properties. Good values for thermal conductivity and heat capacity of explosives at elevated temperatures and particularly in the liquid phase are not available. The thermal conductivity of powdered RDX as used in the experimental programme discussed here has not been measured, and a reasonable value for a powder has been used. However, the calculated times are not very sensitive to changes in the properties, and this is not likely to explain the differences found.

Uncertainty in the thermal transport mechanism. The model assumes that convection does not occur, and that heat transport is purely by conduction. This may be so for the RDX, but it is surely not the case for TNT. Presumably, this will be more important during fast heating when there are greater thermal gradients to drive convection.

Of these, the kinetics and the convection are likely to be the most important. In the absence of sound information, no attempt is made to improve the agreement between the calculations and experiment, because that would be only a curve fitting exercise, and probably applicable only to the composition, heating rate and geometry under consideration.

5.6. Sample Programs

Program for TNT

```
{TNT Medium Scale}
{Values for TNT taken from McGuire and Tarver
  Assumed reaction sequence   A → B
                              A + B → C
                              B + B → C}
TITLE
        "TNT, Medium - soak at 373K, then 3.3 K per hour"

COORDINATES
        ycylinder('R','Z')

SELECT
        thermal_colors on
        errlim=1e-4

VARIABLES
        temp (range = 300, 2000)        {temp – temperature, K}
        aa(range = 0, 1)                {aa - concentration of species A}
        bb(range = 0, 1)                {bb - concentration of species B}
        cc(range = 0, 1)                {cc - concentration of species C}

DEFINITIONS
        {medium scale hardware, dimensions in metres}
        lengthCase = 0.0956   radCase = 0.0245     {o/d cylinder, m}
        radHE = 0.0215                             {i/d cylinder, m}
        thicknessUpstand = 0.0060       {central part of end cap, m}
        thicknessFlange = 0.0080        {flange of end cap, m}
        radCap = 0.0500                 {radius flange, m}
```

```
totalLength = (lengthCase + thicknessFlange)
lengthHE = (lengthCase -2*thicknessUpstand)

heatingRate = 3.3/3600          {degree per second}
h =1                            {heat loss coefficient from ends}

kExpl = 0.24   {thermal conductivity - explosive,  W m^-1 K^-1}
rhoExpl=1700                   {density -explosive,  kg m^-3}
cpExpl= 1400                   {heat capacity - explosive,  J kg^-1 K^-1}

kCase = 40                  {thermal conductivity - steel,  W m^-1 K^-1}
rhoCase = 6700                  {density -steel,  kg m^-3}
cpCase = 500                    {heat capacity - steel,  J kg^-1 K^-1}

Ts = 373                        {soak temperature, K}
Tamb = 300                      {ambient temperature, K}

Q1 = -1.255e5                   {heat of reaction, J kg^-1}
A1 = 1.586e15                   {pre-exp factor - Arrhenius}
E1 = 1.840e5/8.3144             {act energy / R, K }

Q2 = 3.764e6                    {heat of reaction, J kg^1}
A2 = 1.957e11                   {pre-exp factor - Arrhenius}
E2 = 1.443e5/8.3144             {act energy / R, K }

Q3 = 3.889e6                    {heat of reaction J kg^1}
A3 = 2.391e11                   {pre-exp factor - Arrhenius}
E3 = 1.401e5/8.3144             {act energy / R, K }

k, rho, cp        {thermal conductivity, density, heat capacity}
beta              {used to differentiate between case (beta = 0) and
                                                explosive (beta = 1)}
```

```
INITIAL VALUE
        temp = Ts
        aa = 1   bb = 0  cc = 0   {only species A (TNT) present at outset}

EQUATIONS
        del2(k*temp) + beta*rho*(A1*aa*exp(-E1/temp)*Q1 +
        A2*aa*bb*exp(-E2/temp)*Q2 + A3*bb*bb*exp(-E3/temp)*Q3)) =
        rho*cp*dt(temp)
        dt(aa)  = -A1*aa*exp(-E1/temp)
        dt(bb) = A1*aa*exp(-E1/temp) - A2*aa*bb*exp(-E2/temp) -
        A3*bb*bb*exp(-E3/temp)
        dt(cc) =  A2*aa*bb*exp(-E2/temp) + A3*bb*bb*exp(-E3/temp)

BOUNDARIES
        REGION 1 {case}
        k = kCase
        rho = rhoCase
        cp = cpCase
        beta = 0
        start (0,-totalLength/2)
        natural(temp) = 0
        natural(aa) = 0          natural(bb) = 0          natural(cc) = 0
        line to (0, 0) to (radcase,0)
        value(temp)=Ts+HeatingRate*t
        line to (radCase, -lengthCase/2)
        natural(temp)= -h*(temp - Tamb + 1)^1.25
        line to (radCap, -lengthCase/2) to (radCap, -totalLength/2) to
        finish

        REGION 2 {explosive}
        k = kExpl
        rho = rhoExpl
        cp = cpExpl
```

```
        beta = 1
        start (0,-lengthHE/2) line to (0, 0) to (radHE, 0) to (radHE, -
        lengthHE/2)  to finish

TIME    0 to 140000

PLOTS
        for t=113300 by 10 to 140000
        surface(temp) as "Internal Temperature Profile"
        surface(min(1,(1-beta)+(max(aa,0)))) as "Mass Conversion"
        surface(beta*(max(bb,0)))
        surface(beta*(max(cc,0)))
        elevation(temp) from (0,0) to (radCase,0) as "Temp Normal to Axis"
        history(globalmax(temp) - (Ts+HeatingRate*t))
END
```

Program for RDX

```
        {RDX Medium Scale}
        {Values for RDX taken from McGuire and Tarver
        Assumed reaction sequence    A → B
                                     B → 2C
                                     2C → D}
TITLE
        "RDX, Medium - soak at 373K, then 3.3 K per hour"

COORDINATES
        ycylinder('R','Z')

SELECT
        thermal_colors on
        errlim=1e-4
```

VARIABLES

```
temp (range = 300, 2000)      {temp – temperature, K}
aa(range = 0, 1)              {aa - concentration of species A}
bb(range = 0, 1)              {bb - concentration of species B}
cc(range = 0, 1)              {cc - concentration of species C}
```

DEFINITIONS

```
{medium scale hardware, dimensions in metres}
lengthCase = 0.0956   radCase = 0.0245      {o/d cylinder, m}
radHE = 0.0215                              {i/d cylinder, m}
thicknessUpstand = 0.0060           {central part of end cap, m}
thicknessFlange = 0.0080            {flange of end cap, m}
radCap = 0.0500                     {radius flange, m}

totalLength = (lengthCase + thicknessFlange)
lengthHE = (lengthCase -2*thicknessUpstand)

heatingRate = 3.3/3600              {degree per second}
h =1                                {heat loss coefficient from ends}

kExpl = 0.24   {thermal conductivity - explosive,  W m^-1 K^-1}
rhoExpl=1700                        {density -explosive,  kg m^-3}
Hfus = 1.606e+05                    {heat of fusion of RDX, J kg-1}
cpExpl if temp <=476.5 or temp >=477.5 then 1400 else Hfus
                              {heat capacity – explosive,   J kg-1 K-1}

kCase = 40                {thermal conductivity - steel,  W m^-1 K^-1}
rhoCase = 6700                      {density -steel,  kg m^-3}
cpCase = 500                   {heat capacity - steel,  J kg^-1 K^-1}

Ts = 373                            {soak temperature, K}
Tamb = 300                          {ambient temperature, K}
```

```
Q1 = -4.182e5                {heat of reaction, J kg^-1}
A1 = 5.760e19                {pre-exp factor - Arrhenius}
E1 = 1.970e5/8.3144          {act energy / R, K}

Q2 = 1.255e6                 {heat of reaction, J kg^-1}
A2 = 4.740e17                {pre-exp factor - Arrhenius}
E2 = 1.844e5/8.3144          {act energy / R, K}

Q3 = 5.018e6                 {heat of reaction, J kg^-1}
A3 = 1.586e15                {pre-exp factor - Arrhenius}
E3 = 1.426e5/8.3144          {act energy / R, K}

k, rho, cp             {thermal conductivity, density, heat capacity}
beta                   {used to differentiate between case (beta = 0) and
                                    explosive (beta = 1)}

INITIAL VALUE
    temp = Ts
    aa = 1  bb = 0  cc = 0  {only species A (RDX) present at outset}

EQUATIONS
    del2(k*temp)  +  beta*rho*(A1*aa*exp(-E1/temp)*Q1  +  A2*aa*bb*
    exp(-E2/temp)*Q2 + A3*bb*bb*exp(-E3/temp)*Q3)) =
    rho*cp*dt(temp)
    dt(aa)  = -A1*aa*exp(-E1/temp)
    dt(bb) = A1*aa*exp(-E1/temp) - A2*bb*exp(-E2/temp)
    dt(cc) =  2*A2*bb*exp(-E2/temp) - A3*cc*cc*exp(-E3/temp)

BOUNDARIES
    REGION 1 {case}
    k = kCase
    rho = rhoCase
    cp = cpCase
```

```
        beta = 0
        start (0,-totalLength/2)
        natural(temp) = 0
        natural(aa) = 0        natural(bb) = 0        natural(cc) = 0
        line to (0, 0) to (radcase,0)
        value(temp)=Ts+HeatingRate*t
        line to (radCase, -lengthCase/2)
        natural(temp)= -h*(temp - Tamb + 1)^1.25
        line to (radCap, -lengthCase/2) to (radCap, -totalLength/2) to finish

        REGION 2 {explosive}
        k = kExpl
        rho = rhoExpl
        cp = cpExpl
        beta = 1
        start (0,-lengthHE/2) line to (0, 0) to (radHE, 0) to (radHE, -
        lengthHE/2)  to finish

TIME  0 to 140000

PLOTS
        for t=113300 by 10 to 140000
        surface(temp) as "Internal Temperature Profile"
        surface(min(1,(1-beta)+(max(aa,0)))) as "Mass Conversion"
        surface(beta*(max(bb,0)))
        surface(beta*(max(cc,0)))
        elevation(temp) from (0,0) to (radCase,0) as "Temp Normal to Axis"
        history(globalmax(temp) - (Ts+HeatingRate*t))

END
```

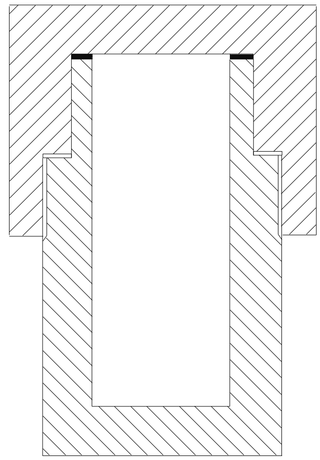
Chapter VI

CONCLUSIONS

A low cost Cook-Off experimental facility has been established at the Royal Military College of Science, Cranfield University, and it was demonstrated that it provides a convenient method of ranking explosives in their response to Cook-Off by the time to event and temperature at event, under two widely different heating rates and at two different scales. This test facility allows for further studies on different parameters influencing Cook-Off of real systems, such as degree of confinement, different materials used in manufacture of cases, heating rates, etc..

A demonstration of suitability for Cook-Off trials with confined explosives was performed on the design of the trials vehicles, based on existing hardware, and it was concluded that this type of design although suitable for these studies imposes a great deal of extra work, namely on the manufacture phase of the test vehicles and also during the preparation of the charges to be trialled, so that confinement and reproducibility of the results can be guaranteed. Additionally, the costs involved in manufacture of a bolt type Cook-Off test vehicle are also considerable.

It is our opinion that a test vehicle like the one presented in the diagram below, in which the cap is fixed with a suitable screw thread, would reduce significantly the amount of work involved in manufacturing of the test vehicles and preparation of the trials phase with the added advantage of significantly reducing the costs involved in manufacturing the test vehicles and man-hours in trials preparation:



The emphasis of the present study was on time to event, and temperature at event, but in addition a qualitative assessment of the violence of the event was made by examination of the fragments of the vehicles, although it is accepted that the relatively light and low cost design of the vehicle may lead to variable confinement in the early stages of the explosive event, and hence to a wider spread of responses than would be obtained from a more heavily confined and more costly vehicle.

The test vehicles used in this study give results which differentiate between the various explosives and explosive mixtures trialled and between the scales.

Results obtained for small and medium scale Fast and Slow Cook-Off trials for RDX/TNT mixtures show, for both scales, and in most cases, a trend for time to Cook-Off and Cook-Off temperatures to decrease with increasing RDX content of the same mixtures.

More experiments are required to establish the reproducibility of these measurements, and to shed some light on the varying kinetics. The design of the equipment makes this a relatively inexpensive undertaking.

A simple heat flow model has been used to gain more insight into the phenomena. This qualitatively indicates the likely sites of self-heating, and the position of thermal runaway leading to explosion. The precision of the quantitative results is limited by the basic assumptions (particularly the lack of convective flow), and by uncertainties in the values of the thermal transport properties, and perhaps most importantly by uncertainties in the decomposition kinetics.

Although the experiment is not designed to assess violence of response, there is an indication that, as would be expected, mixtures with higher RDX content tend to respond more violently, and that response at medium scale is more violent than at small scale. In the firing programme conducted in this study the fragmentation analysis results obtained demonstrate a general pattern of violence of response being more violent for Fast Cook-Off than for Slow Cook-Off thermal profiles. This is in accordance with the observation of Chin & Plooster (1994) that for most high explosives the Fast Cook-Off seems to produce more violent reaction than Slow Cook-Off.

Further work needs to be undertaken in order to explain the exceptional behaviour of some of the tested explosives and to adequately assess and quantify the violence of response of these systems, therefore implying the design and construction of a fully confined test vehicle.

As recommendations for future work, we would like to address the following lines of research:

- perform at least five (5) Cook-Off tests per sample tested in the present study, with the new configuration of the Cook-Off test vehicle above presented, at both heating rates and scales, in order to get a more statistically significant insight into parameters such as time to event, temperature to event and violence of response of these explosive systems;

- scale up further the above Cook-Off test vehicles by the same factor (i.e. 2 kg and 20 kg), to allow for the use of the experimental data to validate models for the prediction of such Cook-Off events in real systems;

- undertake a Cook-Off study with the same set of explosive systems to investigate the influence of the wall thickness of the main body of the test vehicle in the same parameters (i.e. time to event, temperature to event and violence of response). This would mean keeping constant factors like dimensions of the vehicle and heating rate;

- scale up the above experiments by a steady factor (i.e. 0.020 kg, 0.200 kg, 2 kg and 20 kg), to allow further application of the experimental data to validate models used in the prediction of these events and also to contribute for the study of mitigation techniques and devices;

- investigate the influence of using different materials for the casing of the main body of the Cook-Off test vehicles, by keeping constant factors like composition of the explosive system, dimensions of the vehicle and heating rate;

- scale up the above Cook-Off tests by a steady factor (i.e. 0.020 kg, 0.200 kg, 2 kg and 20 kg), to allow for the experimental data to validate models used in the prediction of Cook-Off events in real systems, namely as an input into mitigation studies;

- study the influence of the heating rate on the Cook-Off event of explosive systems, by considering constant factors like composition of the explosive system, dimensions and manufacture materials of the test vehicle;

- research into the influence of heating rate on scaling up studies.

References

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Appendix I

ACCIDENTS DUE TO COOK-OFF EVENTS

The response of the energetic materials in terms of products, heat and pressure generated in response to accidental stimuli varies widely depending on the type and quantity of energetic material subjected to the stimulus.

The hazard offered by an energetic material in a particular situation depends upon its sensitiveness (the level of accidentally applied stimulus necessary to start an event) and its explosiveness (the result of an ignition). Ideally both the sensitiveness and the explosiveness should be low for low hazard. This consideration governs the safety of handling, manufacture, storage and transportation of such systems during their entire life cycle. It is of fundamental importance because the inadvertent explosion of a high explosive ammunition at any stage of its life could be catastrophic. Such accidents may occur in peacetime from non-military causes, and with increased probability in war because of military action.

The list of accidents and their devastating damages either in loss of lives or in damages to equipment is all over the years already too long. Therefore, as an example the following incidents will be described (McQuaide, 1980; Hillstrom, 1985; Boggs & Derr, 1990; Fleming, 1995; Boggs *et al.*, 1998; NIMIC, 2001a, 2001b, 2001c, 2001d; Ramanathan, 2001; BBC News, 2002; NIMIC, 2002):

- **March 12, 1907** - **France** - Accidental ignition of gun propellants in the ammunition magazine aboard ship IENA in dry-dock. Fire and explosions resulted in 117 killed, 33 injured. No estimated cost is supplied for equipment;

- **September 25, 1911** - **Toulon Bay, France** - Accidental ignition of gun propellants in the ammunition magazine aboard ship Liberté. Fire and explosions resulted in the Liberté being lost and 226 people killed, 160 injured;

- **December 12, 1917** - **Nova Scotia, Canada** - A collision between a Belgian boat and a French cargo ship loaded with ammunition, at the entrance of the harbour, caused the rupture of gasoline drums, which caught fire. While the crew was fighting the fire, another boat approached the area. Seeing that the fire was getting out of control, the crew left the boat. 17 minutes later a dreadful explosion occurred that razed the town of Richmond killing 5 000 people and injuring 10 000. Some Indians who were as far as 6 miles away were killed;

- **April, 1926** - **Lake Denmark, New Jersey, USA** - Lighting struck a magazine at the Navy Ammunition Depot, containing 303 912 kg of explosives. Reaction spread. A total of 1.45 million kg exploded resulting in 21 dead and 52 injured. Loss of life would have been worse except the working day ended at noon. The Navy and adjacent Army facilities suffered an approximate $ 75 million loss as well as significant mobilization potential;

- **July 17, 1944** - **Port Chicago, CA, USA** - Three explosions of circa 10 000 tons of munitions resulted in 320 dead and 390 injured, causing major damage within a 1 mile radius and minor damage as far as 25 miles away;

- **November 24, 1944** - **USS Princeton** - Received a single Japanese 250 kg bomb. Fire and explosions destroyed the ship. No information is supplied on estimate cost of damage and/or casualties;

- **January, 1947** - **USA** - A bomb was dropped during handling. The explosion was sympathetically transmitted to 70 tons of bombs in the magazine. As a result 10 people were killed. No information is available on estimate cost for equipment damage;

- **April, 1949** - **Kalvarienberg/Prüm Eifel, Federal Republic of Germany** - Burning of unknown cause on top of a hill (Kalvarienberg) of a store containing about 500 tons of TNT filled ammunition resulted in a disastrous explosion after 1.5 hours. Shortly thereafter a second explosion followed it. The top of the hill (about 250 000 m^3 of soil) was blown away, down to the city of Prüm, covering it with debris and trees. As a result 76 homes were completely destroyed and 161 seriously damaged. As for human losses 60 people were injured and 12 were killed;

- **1950** - **United Kingdom** - At a Royal Naval Ammunition Depot, an explosion of 36 000 kg equivalent of high explosives resulted in stores being destroyed. There is no information concerning the number of fatalities and/or injuries;

- **May, 1957** - **New Mexico, USA** - Accidental dropping of a nuclear weapon from a plane. A chemical explosion resulted on impact. No information is reported on estimate cost of damage and/or casualties;

- **March, 1960** - **Cuba** - Ship board explosion involving 76 tons of weapons' ammunitions, probably due to the dropping of a case of hand grenades. As a result more than 100 people were killed. No information is supplied relating injured people or estimate cost of damage;

- **October, 1960** - **Phoenix, Arizona, USA** - At a salvage yard, a worker using an acetylene torch to cut the case of a HVAR 12.7 cm motor ignited the propellant. Motor went propulsive and travelled 5 blocks and landed on home; broke through exterior walls, and burned hole in living room concrete floor. Motors were supposed to be inert. 5 more motors were found and removed from yard. (6.8 kg UXO). One burned person resulted from this accident. No information on damage to equipment is available;

- **March, 1965** - **Bien-Hoa, Vietnam** - Ammunition dump destroyed by fire and secondary explosions due to a cook-off accident. No fatalities were registered, but materials were destroyed. No information on injured people is supplied;

- **March, 1965** - **Qui Nhom, Vietnam** - Viet Cong attacked an ammunitions' storage area. Fires and secondary explosions resulted in a cook-off incident that left 3 people dead, 34 injured and materials destroyed;

- **1965** - **Da Nang, Vietnam** - Fire and secondary explosions resulted in a cook-off incident with $ 123 million damage in materials destroyed. No information is available on number of casualties;

- **June, 1965** - **USA** - An accident involving a Titan II Missile due to a silo fire from welder arc to hydraulic line resulted in 53 people killed. No information is accessible on number of injured people and estimate cost of damage;

- **June 2, 1966** - **Muiden, Netherlands** - 2400 kg of TNT exploded in a melting shop (Dutch explosives factory KNSF). There was substantial material damage, but no serious personal injuries. Overheating of the melting vessel by steam and impurities in the TNT turned out to be the cause of such an event. No information is obtainable concerning damage to equipment;

- **October, 1966** - **USS Oriskany** - On board ship fire caused by re-stowing aircraft pyrotechnic flares from an aircraft returning from a mission. One sailor dropped a flare and it ignited. A second sailor picked-up flare, and threw it into a locker and closed the door. Unfortunately the locker contained 7 cm rocket warheads; detonation occurred followed by explosion of a liquid oxygen tank. This cook-off accident resulted in 44 people killed, 156 injured and 2 helicopters and 4 aircraft destroyed. $ 15.6 million estimated cost and $ 48 million in ship repairs;

- **May, 1967** - **Utrecht, Netherlands** - Explosion on a ship loaded with 11 tons of ammunition with great damage to surrounding industrial area. Ammunition was obsolete and prepared for dumping. During the handling of pyrotechnic ammunition one of the items must have been activated. As the ship was loaded with all types of ammunition, deflagration from the munitions grew to a detonation of the high explosives munitions also present. This resulted in 2 people dead and 200 injured. No estimate cost of equipment damage is accessible;

- **July 29, 1967** - **USS Forrestal** - An accidental firing of a Zuni rocket from an aircraft being readied for mission set fire to the fuel tank of another parked aircraft across the flight deck, which caused cook-off of the aircraft munitions within minutes. Detonation ruptured flight deck, fuel spilled to lower decks. Bombs, warheads and rocket motors reacted. This cook-off incident resulted in 134 killed, 162 injured, 21 aircraft destroyed, 43 aircraft damaged. Most authors present $ 172 million as estimated cost while a much higher value for the same item of $ 758 million is presented by Boggs *et al.* (1998);

- **1967** - **Elkton, USA** - At Thiokol Elkton two incidents occurred while reclaiming ZAP motor cases, with ferrocene propellant, by hydromining propellant. Two out of four motors ignited this resulting in a change in policy to NOT hydromine ferrocene propellants due to extreme sensitivity to friction or impact. No information on casualties and estimate cost damage is supplied;

- **January 14, 1969** - **USS Enterprise** - Exhaust from an aircraft engine starter unit impinged onto a pod containing Zuni rocket motors: one motor exploded. Fragments ruptured aircraft fuel tanks and a fire resulted. One minute after the first explosion, three more ZUNI rocket motors exploded. Flight deck was ruptured spilling fuel to lower deck. 18 munitions detonated causing 8 holes in flight deck and on board fires. This cook-off incident resulted in 28 people killed, 344 injured, 15 aircraft destroyed and 17 aircraft damaged. $ 57 million estimated cost and $ 487 million in ship repair;

- **March 23, 1969** - **Qui Nhon, Vietnam** - A Viet Cong Sapper team attacked the US ammunitions storage area, causing a fire and secondary explosion of ammunition stacks. As a result 3 people were killed, 34 injured and several tons of ammunition were destroyed (10 000 units of 155 mm artillery shells and 23 700 units of 105 mm shells). No information on estimate cost is given;

- **April, 1969** - **Da Nang, Vietnam** - Fire induced an explosion which propagated to an ammunitions magazine. No information on damage estimate cost and casualties is available;

- **May, 1969** - **Hannover, Linden, Federal Republic of Germany** - Blocked brakes on a running railroad car wheel produced a temperature increase up to excess of 1023 K. Showers of sparks caused smouldering of the railroad car. As the train stopped to fight the fire, 175 mm grenades filled with Composition B, without detonators, exploded probably in the low order. Indications of low velocity detonation (LVD) are: bent and deformed rail car axles and wheels, and unusually large debris of the grenades. This accident resulted in 12 fatalities (8 fireman and 4 railway employees) and 40 people injured. No information on estimate cost for damage is offered;

- **May, 1973** - **Roseville, California, USA** - Explosion over 32 hour period of an ammunition train, 18 freight cars of which were carrying Mk 82 bombs, each loaded with 226.8 kg of high explosives. The initial cause of ignition was ignition of a wooden floor impregnated with sodium nitrate. The train was destroyed and also 140 m of train tracks were lost. Other consequences of this cook-off accident include 48 fatalities and $ 24 million property damage;

- **May, 1975** - **Belgium** - Explosion of a bomb during loading of a wagon. The fire propagated to a wagon filled with TNT located 40 m away. Many wagons were destroyed and 13 people are reported injured;

- **August, 1978** - **Herlong, California, USA** - Detonation of a bomb loaded with a high explosive sympathetically transmitted to 8 others. These bombs were stored between the igloos shaped magazines of the storage area. A nearby igloo was crushed, and its munitions were damaged without reaction. No information is available on estimated cost or casualties;

- **May 26, 1981** - **USS Nimitz** - A crash during landing of an aircraft was followed by a series of explosions. Fuel fire was contained, and order was given to proceed with clean-up operations. One Sparrow warhead underwent delayed detonation and additionally three other warheads detonated before fire was contained. As a result from this cook-off incident 14 people were killed, 48 injured, 3 aircraft destroyed, 9 aircraft damaged and $ 150 million estimated cost in ship damage;

- **August, 1981** - **Zimbabwe** - Explosion of an ammunition magazine, probably due to the explosion of a gas storage bottle, resulted in the destruction of hundreds of tons of ammunition. No information is supplied concerning casualties or estimate cost of damage to equipment;

- **1982** - **Perm, Russia** - Hydromining solid propellant, a SS-24 stage 2 rocket motor ignited on a washout stand. Upon propellant ignition the motor developed enough thrust to eject the motor from the stand and crashed through the walls of the operations building. Motor went propulsive into a nearby dinning hall. The number of casualties is indicated as "several" fatalities and "several" injured people. Hydromining technology development in USSR was brought to a halt as a direct consequence of this accident;

- **November, 1982** - **Tennessee, USA** - At the AF Arnold Engineering Dev. Center, a fire Cell J-4 broke out during Peacekeeper Stage 2 propellant clean-up in the test cell following motor failure. Cutting of damaged, water soaked propellant with piano wire (88% solids AP/Al/HTPB 9072 - 13608 kg propellants consumed). The test cell was destroyed as a consequence and 4 people were killed. No information is offered on the number of injured;

- **May, 1984** - **USSR** - At the Severomorsk Naval Base, fire of unknown origin lead to a series of fires and explosions that lasted for several days. No information is supplied on number and nature of casualties or estimated cost of damage;

- **1985** - **Pavlograd, Ukraine, USSR** - Sympathetic detonation of six Stage 2 SS-24 solid rocket motors, which were on cure cycle. Single motor exploded due to impurities in ingredients. This accident resulted in damage to the buildings and a non-indicated number of fatalities. No indication is given on injured people or estimated cost of damage;

- **August, 1985** - **USA** - During road transport of 10 bombs loaded with 500 kg of TNT a collision occurred, fire broke out and detonation resulted in very large crates. Temporary evacuation of 6000 people. No information is given on estimated cost of damage or casualties;

- **Mid 80's** - **Falklands Islands, United Kingdom** - The HMS Sheffield, a 4100 tons Destroyer, was struck by an Exocet missile. Amidships strike, penetrated fuel tank and smashed into machinery spaces. The warhead did not detonate and the burning propellant ignited fuel fires, resulting in thick acrid acid smoke spreading through the ship's ventilation system. The fire fight lasted 4.5 hours before abandoning ship. Ship sank under tow in heavy seas. The human losses amounted to 20 people killed. No information on injured people and value for estimate cost of damage is available;

- **Mid 80's** - **Falklands Islands, United Kingdom** - HMS Plymouth suffered multiple hits by small bombs. Several fires broke out disabling ship. The ship was destroyed. No information on casualties and value for estimate cost of damage is available;

- **Mid 80's** - **Falklands Islands, United Kingdom** - HMS RFA Sir Galahad endured multiple hits by small bombs. Several fires and disabling bombs caused a runaway ammunition fire leading to the destruction of the ship. 51 fatalities were registered. No information on injured people and value for estimate cost of damage is offered;

- **Mid 80's** - **Falklands Islands, United Kingdom** - HMS Glamorgan was struck by an Exocet missile. A 163 kg warhead did not detonate. The damage included a hanger and helicopter destroyed by fire caused by unspent propellant, shrapnel damage and fire, ship destruction and 13 people killed. No information on injured people and value for estimate cost of damage is available;

- **Mid 80's** - **Falklands Islands, United Kingdom** - HMS Antelope was struck by a bomb, which did not detonate. Nevertheless, fires caused by the bomb detonating while attempting to defuse. Runaway munitions fire destroyed the ship. No information on casualties and estimate cost of damage is accessible;

- **May, 1987** - **USS Stark** - Hit by Exocet missiles while operating in Persian Gulf. Missile warhead did not detonate. Nevertheless, missile penetrated about 2438 cm inboard. Fire resulted: 54 kg burning solid propellant at 1922-2200 K. Heat, acid vapours, and smoke filled surrounding area impeding escaping personnel from compartments. Second missile hit, penetrated hull and detonated 152 cm inboard. Detonation ripped large hole in hull accelerating combustion of burning materials. Port side fireman lost in blast. Vertical fire spread into compartments directly above main blaze. Several injuries are reported and 37 fatalities occurred. No value is obtainable for the estimate cost in equipment damage;

- **May 4, 1988** - **Henderson, Nevada, USA** - At the PEPCON AP Plant more than 3.63 million kg of ammonium perchlorate burned and detonated killing 2 people and injuring more than 350 local residents. The damage caused is estimated to exceed \$ 73 million;

- **June, 1989** - **California, USA** - At Aerojet, a fire broke out during high pressure water-jet propellant removal operation with Minuteman 2nd Stage. A faulty purge water flow subsystem in water-jet removal system caused friction on propellant that had accumulated in boom bearing block. (5443 kg Class 1.3 propellants). Moderate damage was induced in the equipment and there were no human losses or injuries;

- **September, 1990** - **California, USA** - At Edwards Air Force Base, a Titan IV SRMU fire started after ground impact during movement by crane near test strand. Crane tipped over due to unstable working surface. Motor impacted the ground and skid down test stand flame bucket. Ignition most likely resulted from impact. The propellant composition ignited was AP/Al/HTPB. The damage to equipment included test stand, crane and several nearby buildings destroyed with an estimated cost of \$ 9 million. No information on casualties is offered;

- **August, 1994** - **White Oak, USA** - At Naval Surface Warfare Center nearly 1950 kg of explosives housed in magazine sited for 3629 kg exploded. Six people were in the vicinity and no injured were registered. It was definitely a detonation as evidenced by extreme rubbelization of concrete and large crater in the ground. Explosion supposedly heard 16 km away. Some firebrands and small grass fires broke out. Damaged included broken windows, no debris outside of hazard arcs, magazine and respective contents were destroyed. There were no injuries or fatalities. Cause of this accident is indicated as improper/careless storage;

- **1995** - **Persian Gulf** - In Operation Desert Storm a SCUD missile landed near stored ammunition. It was not a direct hit, but it resulted in a Cook-Off accident. No information is supplied on damage to equipment and casualties;

- **1995** - **Persian Gulf, Kuwait** - In Operation Desert Storm, at Camp Doha, there was a transport vehicle fire. Fire spread and secondary explosions resulted. More tanks were lost in single incident than in the entire Desert Storm conflict due to this

Cook-Off accident. Further damage includes materials stored at Camp Doha, 52 people killed and 3 injured. Injuries occurred while clearing damaged ordnance. No value on estimated cost for damage is available;

- **June 18, 1998** - **Losiny, Ural Mountains, Russia** - An Army munitions depot was struck by lightning and 14 servicemen were killed. Several others are reported missing. A forest fire resulted covering an area of more than 150 hectares, forcing thousands of villagers to leave their homes. No further information was offered;

- **May 9, 1999** - **Kargil, Kashmir, India** - An ammunition dump held thousands of shells for field guns, multi-barrelled launchers, mortars and howitzers. Infiltrators fired a few rockets into the dump causing a fire which destroyed 40 000 to 50 000 rounds of artillery in a tremendous blast. No further information was offered;

- **October 9, 1999** - **near Mazar-e-Sharif, Afghanistan** - A series of explosions at an arms dump in northern Afghanistan resulting from ammunition being loaded into a truck on the road to Shibergan. The blast caused a fire, which took two hours to control, while series of small explosions occurred at the site. Human losses amount to 7 people killed and several civilian and military injured;

- **April 28, 2000** - **Bharatpur, India** - At an Army ordnance depot a massive fire broke out. The ammunition stored comprised air defence missiles, anti-tank guided missiles, artillery ammunition, ammunition for tanks, small arms ammunition, mines and explosives. The continuous explosions thwarted attempts by the emergency services to reach the seat of the blaze. Some of the explosions have been described as "immense". The ammunition stored in 20 open plinths and 9 affected sheds weighing approximately 12111 tons and costing 3.76 billion rupees ($ 80 million) was lost. The fire was eventually contained the next day by which time it had caused damage to around 20 surrounding villages. Some of the villages were evacuated and the efforts to recover unexploded and semi-exploded ordnance from the areas surrounding the depot took several days. As a result of this accident 2 people were killed and 10 injured when missiles, shrapnel and splinters from exploded ordnance ammunition showered down on villages up to six kilometres from the base. The extremely high temperatures of the pre-monsoon season could be the cause for this accident;

- **April 29, 2000** - **Pathankot, Punjab, India** - At an Indian Army ordnance storage facility a devastating fire broke out resulting in the destruction of many tons of live artillery shells, tank ammunition and related military hardware. Series of deafening explosions ("more than 500 separate blasts during the first hour after the fire started"), sending shockwaves across several kilometres were reported. The areas in the proximity of the ammunition dump were fled and 5 villages were evacuated. The fire lasted 4 hours before being brought under control. Authorities confirmed that nearly 500 tons of heavy ammunition was destroyed: an open ammunition store comprising 125 mm tank ammunition, 155 mm howitzer shells, and related military hardware was lost. A preliminary assessment put the estimate loss cost at more than $ 3 million. Rising summer temperatures are indicated as the cause as they have been known to heat up explosives stored in the open and obsolete and unstable ammunition stored at such dumps is at great risk of spontaneous combustion. No information was provided on casualties;

- **March 3, 2001** - **Conakry, Guinea** - A fire started a series of explosions at an ammunition dump at an Army base. At least 10 people were killed. No further information was offered;

- **May 20, 2001** - **Al-Bayda, Yemen** - At an arms market in central Yemen a blast, apparently resulting from the spontaneous explosion of dynamite in a warehouse, took place. As a result 14 people were killed and 19 injured. The blast destroyed the building and several warehouses and stores. Official reports say that the dynamite that caused the explosion belonged to a businessman who sold it for civilian use, such as road construction. No additional information available;

- **June 8, 2001** - **Hoa They, Vietnam** - Explosion of 3.5 tons of explosives and ammunition blew up an Army warehouse, resulting in 4 people injured and about 100 homes badly damaged;

- **June 8, 2001** - **Ramenskoye, Russia** - Fire in one of Russia's S-300 air defence missile systems destroyed 3 launchers and 12 missiles, but no personnel injuries were reported. Russian officials stated that the fire erupted during an equipment check and blazed for 3 hours before being extinguished. Eyewitnesses stated there had been explosions and debris hurled up to half-mile from the base. A short-circuit in one of the missiles seems to be at the origin of these accident according to news reports;

- **June 25, 2001** - **Chita, Russia** - A Russian Army ammunition dump caught fire after being hit by lightning. Continuing explosions forced the authorities to evacuate 10 000 residents from around the base. One officer was reported injured by exploding antitank-shells. Shells were found as far as 8 km from the burning Army base;

- **July 11, 2001** - **Darulaman, Afghanistan** - At an ammunition depot an explosion injured 3 people. The ammunition depot was destroyed. No other details were obtainable;

- **July 14, 2001** - **Southport, New Carolina, USA** - The ammunition ship SS Edward Carter, a 290 m contract vessel that hauled ammunition and other cargo, caught fire at an Army terminal. The fire started in the engine room and as a result 2 people died. The blaze was confined to the engine room and no other casualties were reported, the situation being contained by midnight. Cause undetermined so far;

- **July 21, 2001** - **Buryat, Siberia, Russia** - Fire broke out at an Army ammunition depot due to lightning. As a result 3 people were killed and 4 injured. No other information was available;

- **August 8, 2001** - **Balkhash, Karaganda, Kazakhstan** - Fire swept through a depot holding most of Kazakhstan military's ammunition. Reports mentioned explosion of shells and rockets flying for several kilometres. A village had to be evacuated, but there are immediate reports of personal injury. Damage to other equipment (power line providing electricity to water pumps at the Lake Balkhash) resulted in the interruption of supplies of water to Balkhash;

- **August 16, 2001** - **Katpadi, Tamil Nadu, India** - An explosion at a government-owned dynamite factory killed at least 25 people and seriously injured another 3 people. At least 30 people were inside the factory at the time of the explosion. Fire broke out and took several hours to be controlled. This factory produced nitrate explosives and detonators used in mining and quarrying. Accidental ignition of unspecified origin was pointed as the cause. No further information accessible;

- **September 21, 2001** - **Toulouse, France** - At the Azote de France (AZF) fertilizer plant, from the group TotalFinaElf, an explosion killed 30 people and injured more than 2000, leaving more than 11 000 homes, university, school and public buildings without window panes and with weakened structures. Allegations were made by the La Depeche du Midi, a newspaper in Toulouse, that the ammonium nitrate that caused the explosion was stacked "in a real dump" with minimal surveillance and security, and of "incredible negligence";

- **September 27, 2001** - **Pindad, Java, Indonesia** - The ammunition dump of the Indonesian Army's firearms manufacture PT was highly prone to explosions. At least 1 person was killed. No probable cause is known, but it may have occurred during a drying process involving wet explosives. There is no information on damage estimate cost;

- **October 3, 2001** - **West Virginia, USA** - **(Near Miss)** A truck carrying 19051 kg of B-Grade explosives crashed. According to officials quoted, "the driver lost control during a coughing fit after a sip of coffee". Surrounding areas were evacuated. No ignition happened due to the fact that the explosives landed on the grass and not on asphalt;

- **October 15, 2001** - **Las Vegas, Nevada, USA** - At Aero Tech Inc. an explosion at a hobby rocket company injured 8 people, 2 critically, and forced the evacuation of residents within a 700 m radius due to the release of hazardous chemicals. Three fire fighters were treated for smoke inhalation and released. About 1134 kg of ammonium perchlorate and 363 kg of magnesium were stored in the warehouse. No information on estimate cost of damage is available;

- **October 25, 2001** - **Pak Chong, Nakhon Ratchasima, Thailand** - An accident in a 395 acre arsenal, a major artillery supply base for Thailand's north-eastern region, resulted in 7 of the 44 weapon stores to be completely destroyed and 15 other weapon stores damaged by chain reaction explosions. The munitions involved were not Insensitive Munitions (IM): anti-tank mines type 67 (HE: Comp B), landmines, bangalore torpedoes, artillery shells, mortars, rockets, gun propellants and small-arms ammunition. Material losses involve also 8000 houses damaged by the explosions that lasted 10 hours. Human losses involved 19 deaths and 90 injured. Further details of this accident are provided by NIMIC Newsletter 4th Quarter (2001) and a report by P. Marchandin edited by NIMIC (2001);

- **December 24, 2001** - **Kargil, Kashmir, India** - Indian soldiers shelled Pakistani positions destroying 2 ammunition dumps. A mortar shell hit the fuel, oil and lubricants (FOL) depot causing an extensive fire that initiated mines laid in no-man's land and stored in bunkers nearby. All men fled to safety. No further information on casualties or damage estimate cost is offered;

- **January 11, 2002** - **Bikaner, Rathasjan, India** - During the transfer of heavy ammunition from Bathinda in Punjab to Garanganar-Bikaner in north frontier of Rathasjan an electric spark from one of the trucks triggered massive explosions in the parked convoy. As a result nearly 70 explosives-laden trucks out of the 235 used to move the ammunition caught fire and about 1000 tons of ammunitions were lost. Shells, rockets and wreckages landed in civilian areas in an 8 km radius. Almost 50 incidents were reported in the city at 3 km distance from the site of the explosions (one at the hospital). Consequently, 2 civilians were killed (one employee of the local hospital) and 12 injured when missiles hit buildings in the city. No official information was available on the number of casualties in the depot. Much live ammunition was found in the Udasar urban area. Around 40% of the ammunition recovered from 100 localities during a week cleanup operation was live;

- **January 27, 2002** - **Lagos, Nigeria** - A fire spread to an armoury, possibly via a nearby petrol station, and caused an explosion within minutes. Ten minutes later dozens of explosions sent artillery munitions hundreds of meters into the sky and across the city. Eyewitness reported that the explosions shattered high-tension wires and electric cables with devastating consequences on the surrounding areas. The explosions reverberated 30 km away causing considerable damage, shattering windows and doors as far as 10 kilometres away at the international airport. The explosions and fire continued until the early hours of the day after.

The weapons stockpile included a large amount of heavy artillery ammunition returned to Nigeria following peacekeeping missions in Liberia and Sierra Leon. Officials placed the human losses in 700 fatalities; a senior military source estimated the cost at about $ 12 million worth of ammunition lost. Official sources referred two additional problems that could help to justify the dimensions of this accident: no quality control on the type of armament acquired over the years from the most various origins and poor storage conditions.

In the examples mentioned, it is important to notice that most of the incidents occurred during normal peacetime operations, thermal effects being the main type of stimuli causing the accidents.

Another case study on matters related with the energetic materials safety is the civil pyrotechnic industry, in countries with very old traditions in this field such as

China, Taiwan, Portugal, Mexico, etc.. The occurrence of severe accidents is due mainly to the very severe thermal cycles that the energetic materials are submitted to during the manufacturing process. Nevertheless, one has to mention that poor handling procedures have to be added to this situation. Another major player in the accidents occurring with this type of materials has to be the very poor or non-existent safe storage conditions adopted in most of the abovementioned countries.

Appendix II

ASSESSMENT OF BLAST DAMAGE

The software BlastXW – Explosions Inside Multiple Structures (Version BlastXW 3.6.3.1), supplied as part of the Protective Structures Analysis and Designing System (PSADS) CD-Rom (PSADS, 1998), was used in order to assess the capability of the bunker and the fragment containment box to sustain the most violent blast response possible of the explosive systems to be tested in this study.

Two study case scenarios were run, for both scales, for detonation of 100% RDX (most violent) and deflagration of 100% TNT (less violent).

For the case of the fragment containment box, some calculations were also performed with another software code CONWEP, which stands for "CONventional WEaPons effects". A discussion of the results obtained with both routines is offered.

As these results did not provide a value for the maximum explosive load to cause failure of the fragment containment box it was necessary to perform further calculations using the SpAnw software code (Defence Special Weapons Agency – Version 1.0), also supplied as part of PSADS, using as pressure loads the results obtained with BlastXW for a range of RDX loads of 0.2 - 1 kg. These results are also presented and discussed.

The blast results obtained for the bunker are included and analysed here.

A.II.1. FRAGMENT CONTAINMENT BOX

A.II.1.1. BlastXW

This software code calculates the effects of explosions within structures. It evaluates the pressure-time histories at "target points" defined within the structure produced by the explosion of different materials.

The fragment containment box was input in the calculations as Room 1 and the targets considered were: the permanent opening immediately above the explosive charge and the point on the side of the box closest to the explosive charge (Fig. AII.1).

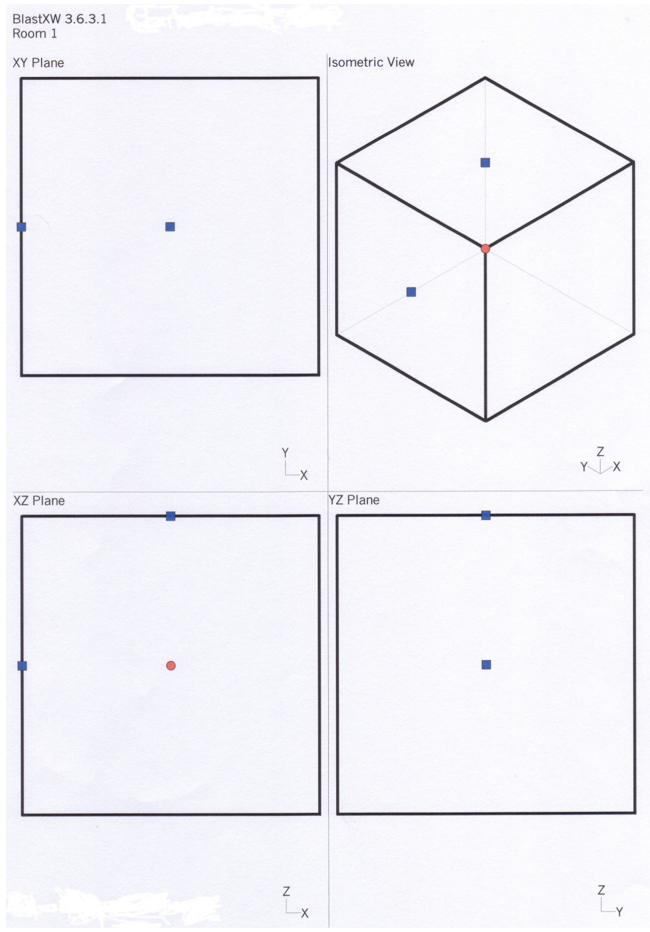

Figure AII.4 - Target Points (Squares) and Explosive Charge (Circle) for the Fragment Containment Box.

The results obtained are summarised below:

Parameter	TNT 0.02 kg	TNT 0.20 kg	RDX 0.02 kg	RDX 0.20 kg
First Pressure (MPa)	6.5	41.3	7.1	44.1
Peak Pressure (MPa)	6.5	41.3	7.1	44.1
Min. Pressure (MPa)	1.7 E-04	1.7 E-04	1.7 E-04	1.7 E-04
Peak Impulse (MPa.s)	1.0 E-02	4.5 E-02	7.9 E-03	5.5 E-02
Det. Gas Pressure (MPa)	7.1 E-01	2.5	4.9 E-01	3.343

Table AII.1 - Parameters Calculated for TNT and RDX Charges.

These results show the expected evolution of blast pressure: increasing values, for both scales, from TNT to RDX.

A typical pressure vs. time history is presented below, which shows a series of reverberating blast waves in the initial part of the trace followed by the decaying gas pressure:

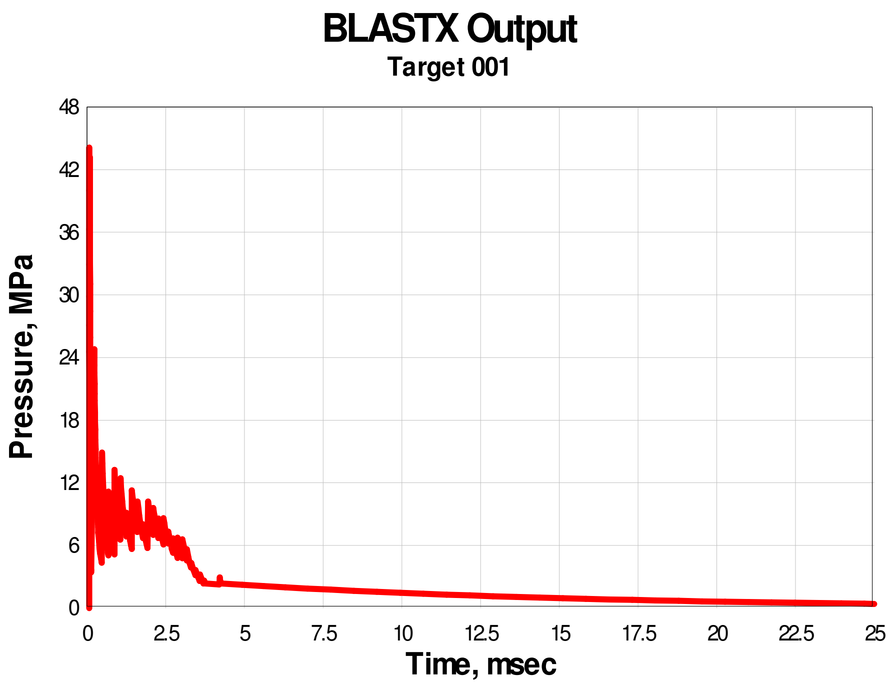

Figure AII.5 - Typical Pressure vs. Time History.

A.II.1.2. CONWEP

This software code calculates the blast wave resultant produced by spherical free air-burst from an explosive of given type and mass. Consequently, the effects of the structure in terms of reflection and further amplification of the pressures are not accounted for.

For these calculations the standoff distance of the charge used is the distance from the centre of the fragment containment box to the wall of the box. Thus, the pressure obtained is the first reflected pressure on the containment box wall. CONWEP does not have the capability to evaluate subsequent reflections.

This code is considered to be an accurate tool for estimating the initial pressure load on this structure and is based on a large amount of experimental data as the results of the calculations performed with CONWEP are normally confirmed by free field experiments.

For the present study the results obtained are presented in Table AII.2:

Parameter	TNT 0.02 kg	RDX 0.02 kg	TNT 0.20 kg	RDX 0.20 kg
Equivalent Weight of TNT (kg)	2 E-02	2.23 E-02	2 E-01	2.23 E-01
Range (m)	0.25	0.25	0.25	0.25
Peak Pressure (MPa)	6.34	7	42.59	45.89
Impulse (MPa.ms)	0.17	0.18	1.07	1.2
Time of Arrival (ms)	0.123	0.12	6.97 E-02	6.8 E-02
Duration (ms)	0.47	0.46	0.144	0.143
Decay Coefficient	2.84 E-02	2.79 E-02	3.23 E-02	3.31 E-02

Table AII.2 - Parameters Calculated for TNT and RDX Charges, Using CONWEP.

Similarly, these results demonstrate that, for both scales:

- blast pressure increases from TNT to RDX;
- duration of the blast presents a reduction from TNT to RDX.

A comparison of the results obtained with BlastXW and CONWEP for the same explosive loads shows a difference in the results obtained for the first pressure. Theoretically these should be the same as both codes use essentially the same criteria. However, these differences can be related to the difference on the input parameters, such as the geometry of a complete arrangement (BlastXW) and a spherical free air-burst (CONWEP).

The calculations with both software codes do not provide on their own a value for the maximum explosive load that will induce failure of the fragment containment box.

As direct calculations of the maximum mass of explosive that will induce failure of such a structure are rather difficult (Edwards, 2002; Smith, 2002; Rose, 2002), and due to the impracticality and to minimise the costs of assessing the mass of explosive needed by direct testing for failure of the fragment containment box, an indirect method was devised. The method adopted involved monitoring of maximum displacement of the structure for increasing blast loads.

A selection of the RDX charge masses was made starting with worse case for this study: 0.2 kg, 0.225 kg, 0.25 kg, 0.30 kg, 0.35 kg, 0.40 kg, 0.50 kg, 0.75 kg and 1 kg RDX.

Calculations using BlastXW were performed for all these RDX charges and used as pressure-time histories in further calculations performed by means of the PSADS-SpAnw code. This code provided the values for the Ductility Factor (μ) and the Maximum Support Rotation. By studying the evolution of these it is possible to determine when a structure entered the plastic regime producing permanent and irreversible structure deformation.

Mays & Smith (1995) indicate a value of 12 degrees for the rotation angle at a support of a reinforced concrete structural element in civil engineering applications. Under these conditions the structural element will have undergone considerable plastic deformation. This situation corresponds to a ductility factor of approximately 20 for a structural steel element. These values were used to define acceptable upper limits of response.

The values obtained with BlastXW are presented below:

Parameter	**0.20 kg**	**0.225 kg**	**0.25 kg**	**0.3 kg**	**0.35 Kg**	**0.40 kg**	**0.50 kg**	**0.75 kg**	**1 kg**
P_{First} (MPa)	44.1	47.7	51.2	57.7	63.6	69.1	79.3	100.8	118.7
P_{Peak} (MPa)	44.1	49.2	51.9	57.7	63.6	69.1	79.3	100.8	118.7
P_{Min} (MPa)	1.7 E-04	1.7 E-04	1.7 E-04	1.7 E-04	-1.3 E-04	1.7 E-04	1.7 E-04	-1.3 E-04	1.7 E-04
Peak Impulse (MPa.s)	5.5 E-02	6 E-02	6.5 E-02	7.5 E-02	8.6 E-02	9.6 E-02	1.2 E-01	1.7 E-01	2.1 E-01
$P_{Det.\ Gas}$ (MPa)	3.3	3.6	3.9	4.5	5.1	5.7	6.8	9.7	12.7

Table AII.3 - BlastXW Results for Different RDX Loads.

The results obtained with PSADS - SpAnw are presented in Table AII.4:

Parameter	**0.20 kg**	**0.225 kg**	**0.25 kg**	**0.3 kg**	**0.35 Kg**	**0.40 kg**	**0.50 kg**	**0.75 kg**	**1 kg**
Maximum Support Rotation (degrees)	1.7	2.1	2.5	4.8	12.8	27.1	55.2	80.3	85.7
Ductility Factor	1.2	1.5	1.7	3.4	9.0	20.2	56.6	229.3	520.7

Table AII.4 - PSADS - SpAnW Results for Different RDX Loads.

The plot of the ductility factor vs. charge mass is shown in Figure AII.3:

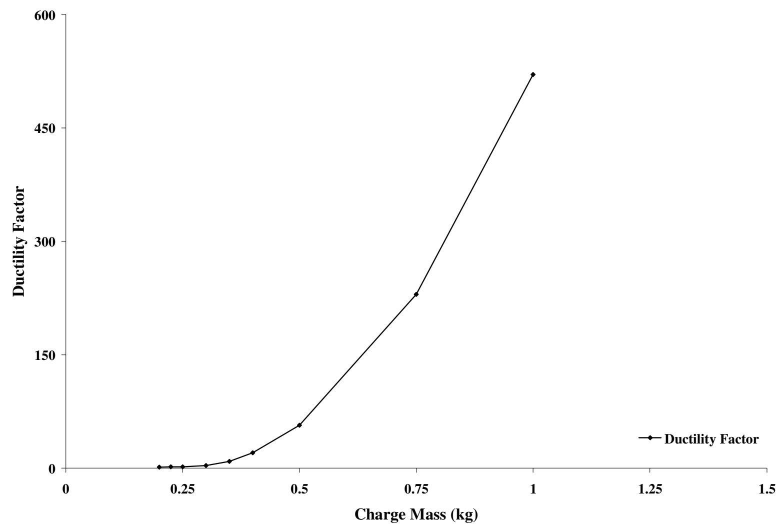

Figure AII.6 - Ductility Factor vs. RDX Charge Mass.

The results for the 0.225 kg RDX mass show a ductility factor higher than 1 indicating that the fragment containment box just started to yield. The 0.25 kg RDX charge presents a situation close to the plastic deformation region. It is for the 0.30 kg and 0.40 kg RDX charges that results indicate that yielding of the material is occurring.

It is important to notice that with yielding there is an increase in deflection, which is also verified by the results on Table AII.4.

Displacement history plots were obtained for every RDX charge considered. In Figures AII.4 and AII.5 two examples are offered.

The analysis of the displacement history plots obtained with the same software clearly shows that for a 0.20 kg RDX load the response obtained by blast is elastic, with sinusoidal oscillations with a small mean displacement indicating little plastic deformation. For higher loads, the permanent plastic deformation increases, with an overlaid elastic behaviour.

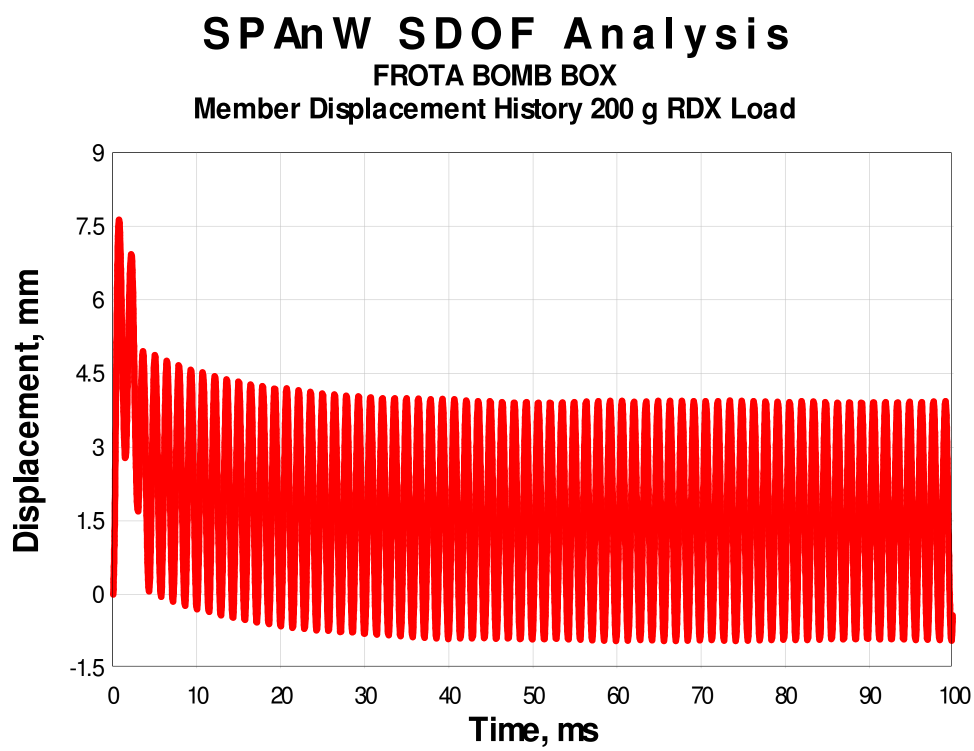

Figure AII.7 - Displacement-Time History for a 0.20 kg RDX Charge.

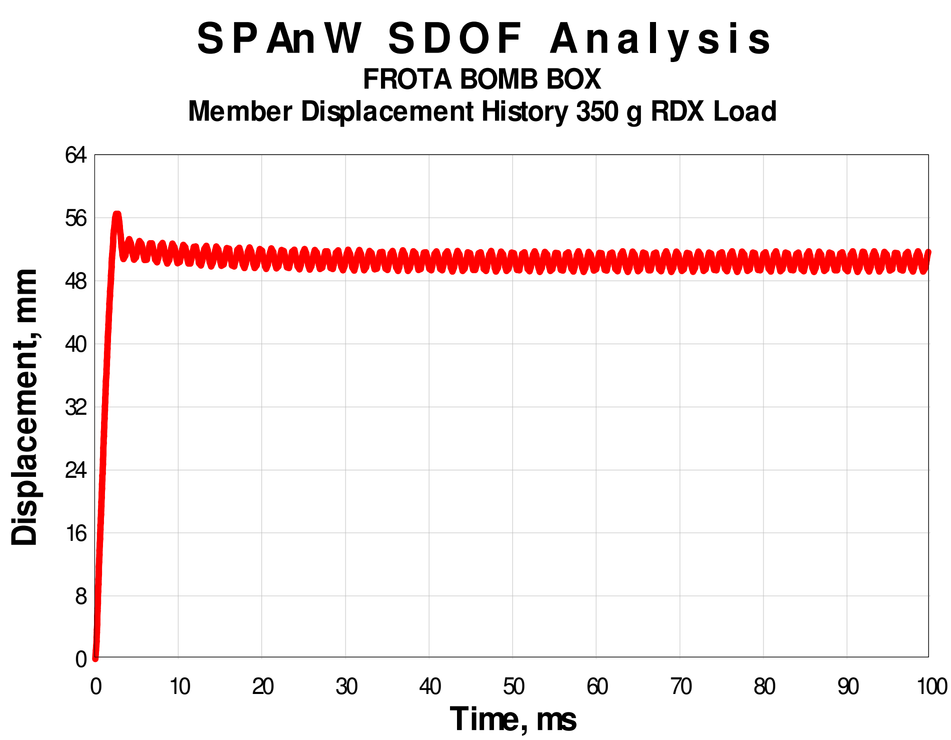

Figure AII.8 - Displacement-Time History for a 0.35 kg RDX Charge.

It is important to remember that these results were obtained by means of a lumped mass equivalent system of the plate with built-in supports along all four sides as a single degree of freedom, assuming uniform loading over the plate surface. This loading was obtained from the “worse case” scenario: a spherical charge of explosive in the centre of the fragment containment box and a target point on the wall of the box closest to the charge.

By use of a single degree of freedom approach, PSADS-SpAnW is a conservative simulation model, in a sense that it overestimates the effect of the load on the structure, constituting a very useful tool for designing purposes.

This implies that in reality a larger explosive charge (larger than 0.35 kg RDX) can be detonated before failure is induced in the fragment containment box (Smith, 2002).

Nevertheless, it is important not to forget that the effect of the blast on the structure of the fragment containment box in the plastic response regime is cumulative and so, after a large number of trials it is expected that failure might occur at this charge level.

Another aspect related with the energy associated with the blast of an explosive load, is the fact that in confined charges hence blast occurs part of the energy is certain to be involved in the fragmentation of the case and another part is due to accelerate the fragments originated from the case rupture. This energy will not therefore be available to the blast wave.

The blast effect of a confined explosive charge is reduced compared to that of a bare charge (see for example Davies, 2001). To assess the correct overpressure the equivalent bare charge has to be computed, usually with the equation:

$$W_b = 1.19\left[\frac{1+M_r(1-M_c)}{1+M_r}\right]c \qquad \text{[AII.1]}$$

where c is actual charge weight, W_b is the equivalent bare charge, M_r is the ratio of case weight (m) to charge weight (m), and M_c = 1 when M_r > 1 and = m/c when M_r <1.

In this study, the worst case scenario is a medium scale 100% RDX charge, where $M_r = 6.07$, $W_b = 0.17c$, i.e., about 83% of the energy of the explosion is used in disrupting and accelerating the case.

Once the disruption of the case took place, fragments will be accelerated in all directions. The average fragment velocity can be determined by means of Gurney's equation. According to Davies (2001), Gurney considered that the energy available from the explosive is portioned between the kinetic energy of the detonation products and the kinetic energy of the fragments of the case. For different simple geometrical shapes, Gurney derived an equation for the initial static velocity of the fragments:

$$V_0 = \sqrt{2E}\sqrt{\frac{\mu}{1+k\mu}} \qquad \text{[AII.2]}$$

where $\sqrt{2E}$ is the Gurney constant (different for each explosive), μ is the ratio of the mass of the explosive to the mass of the case, k is a constant for the geometry (k = 0.5 for an infinitely long cylinder or for cylinders with L/d > 2).

In the present study case, the Gurney constant for RDX is 2451 ms^{-1}, μ is 0.165. It is assumed as a rule of thumb (e.g. see Davies, 2001) that the ability of a fragment to penetrate a steel target is related to its kinetic energy density (kinetic energy divided by the penetrating area). It is generally considered that KE density of 100 J mm^{-2} will penetrate 10 mm steel, and 250 J mm^{-2} will penetrate 30 mm steel.

Assume that the fragments are cubes of size equal to the thickness of the case (3 mm). Density of steel is 7600 kg m^{-3}, so each fragment has a mass of 2.05×10^{-4} kg.

The area of each side is 9×10^{-6} m^2. The KE density of a fragment is, therefore,

$$\frac{\frac{1}{2} * 2.05 * 10^{-4} * 956^2}{9 * 10^{-6}} = 10.4 * 10^6 \text{ J m}^{-2} \equiv 10.4 \text{ J mm}^{-2} \qquad \text{[AII.3]}$$

So, these small fragments are incapable of penetrating the box.

Consider a more severe case that of an end cap impacting edge on at the same velocity. If the mass of the end cap = 0.085 kg; area over which penetration occurs (assumed a rectangle of size) is (diameter of cap) x (thickness of cap) = 12.6×10^{-4} m^2:

$$\text{KE density} = \frac{\frac{1}{2} * 8.5 * 10^{-2} * 956^2}{12.6 * 10^{-6}} = 31\,\text{J mm}^{-2} \qquad \text{[AII.4]}$$

The fragment will not penetrate the containment box, but it may well do considerable damage to the structure of the box and weaken it.

The errors incurred in these calculations are due to the reduced dimensions of the cylinder and the low density RDX used resulting in low velocity values.

For safety reasons, a final recommendation on the explosive charge that will induce failure on the fragment containment box is that it should be less than 0.50 kg of RDX, i.e., 0.55 kg of equivalent TNT for cook-off trials. Reasons for this are:

- the model indicates that failure yielding of the fragment containment box is induced by little less than 0.35 kg RDX loads;
- the model overestimates the effect of load on the structure;
- 83% of energy of the blast wave is diverted to the case disruption and acceleration;
- the damage of the charge casing fragments impacting on the containment box inside walls is not accounted for in codes like BlastXW;
- the fragments will be contained;
- damage has a cumulative effect.

A.II.2. BUNKER

In the blast calculations, by means of BlastXW code, the bunker was input as Room 2 and the targets considered were: the point on the roof immediately above the fragment containment box and the most distant wall within the bunker (Figure AII.6).

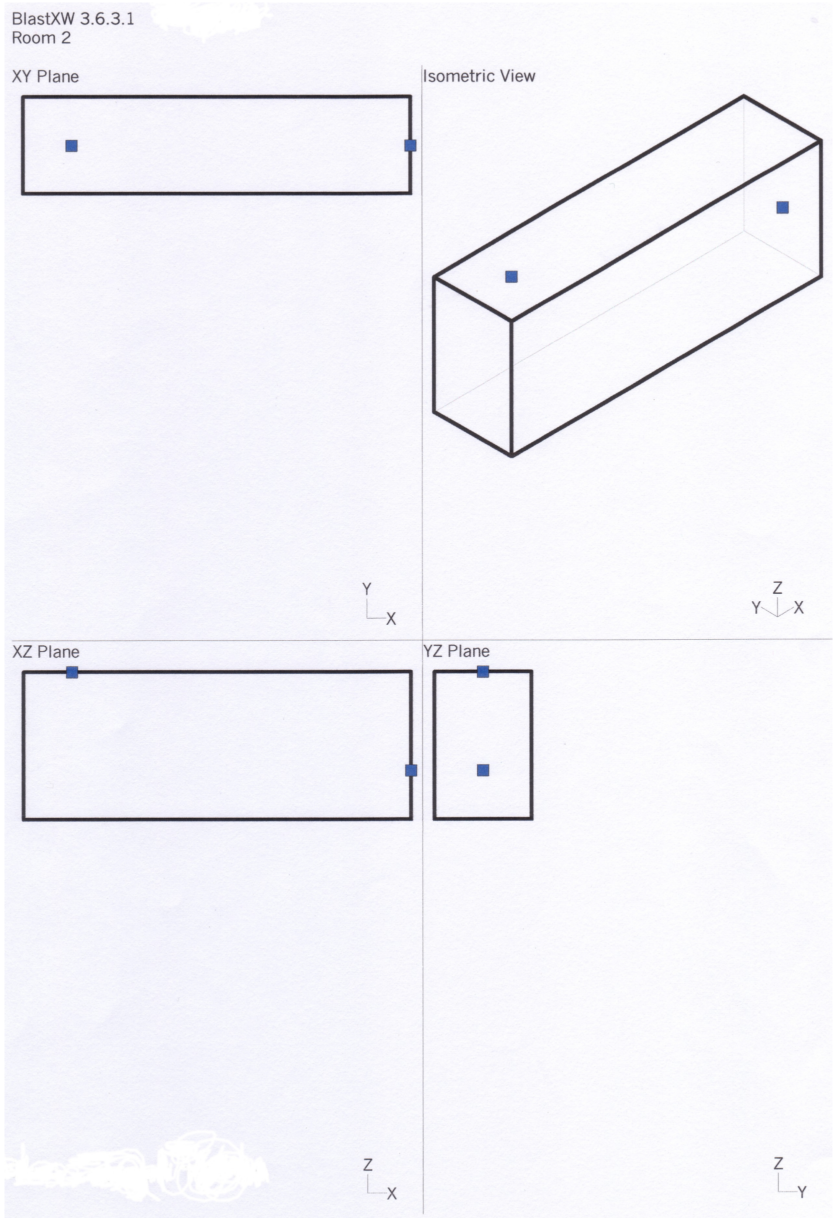

Figure AII.9 - Target Points (Squares) for the Bunker.

The results obtained are presented below:

	TNT 0.02 kg		TNT 0.20 kg	
Parameter	**Room Roof**	**Room End**	**Room Roof**	**Room End**
First Pressure (MPa)	3.4 E-03	7.7 E-04	7.5 E-03	1.4 E-03
Peak Pressure (MPa)	9.1 E-03	3.6 E-03	2.0 E-02	5.8 E-03
Min. Pressure (MPa)	-8.0 E-03	-4.2 E-03	-1.4 E-02	-7.1 E-03
Peak Impulse (MPa.s)	8.2 E-06	3.6 E-06	2.4 E-05	1.4 E-05
Det. Gas Pressure (MPa)	1.7 E-04	1.7 E-04	1.7 E-04	1.7 E-04
Fill Gas Pressure (MPa)	6.2 E-05	6.2 E-05	1.6 E-04	1.6 E-04

Table AII.5 - Parameters Calculated for TNT Charges.

	RDX 0.02 kg		RDX 0.20 kg	
Parameter	**Room Roof**	**Room End**	**Room Roof**	**Room End**
First Pressure (MPa)	4.0 E-03	9.3 E-04	8.5 E-03	1.4 E-03
Peak Pressure (MPa)	1.1 E-02	4.6 E-03	2.2 E-02	6.7 E-03
Min. Pressure (MPa)	-7.9 E-03	-4.0 E-03	-1.9 E-02	-8.6 E-03
Peak Impulse (MPa.s)	8 E-06	5 E-06	3.3 E-05	1.7 E-05
Det. Gas Pressure (MPa)	1.7 E-04	1.7 E-04	1.7 E-04	1.7 E-04
Fill Gas Pressure (MPa)	7.2 E-05	7.2 E-05	2.6 E-04	2.6 E-04

Table AII.6 - Parameters Calculated for RDX Charges.

The bunker has been designed to withstand detonations of 1 kg explosive charges. Therefore, the use of explosives charges of 0.20 kg of RDX on a fragment box will have no detrimental effect on such a structure.

Appendix III

COOK-OFF PROFILES

The cook-off profiles obtained for the two different firing programmes established for this study are presented in the following figures:

- Fast Cook-Off
    - Small Scale: Figures AIII.1 - AIII.9
    - Medium Scale: Figures AIII.10 - AIII.17
- Slow Cook-Off
    - Small Scale: Figures AIII.18 - AIII.24
    - Medium Scale: Figures AIII.25 - AIII.31.

The sampling rate was normally one data point per 15 s. However the small scale RDX, the first set of measurements to be obtained, was sampled at one data point per minute, because the duration of the experiment could not be predicted with accuracy, and might have exceeded the storage capacity of the data logger.

In the figures: TC 1 = Centre Thermocouple and TC 4 = Wall Thermocouple.

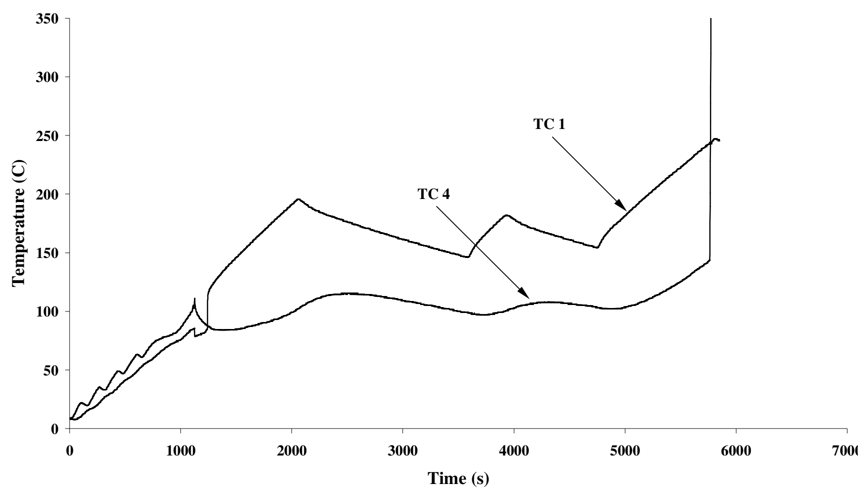

Figure AIII.1 - Small Scale Fast Cook-Off of a TNT Charge.

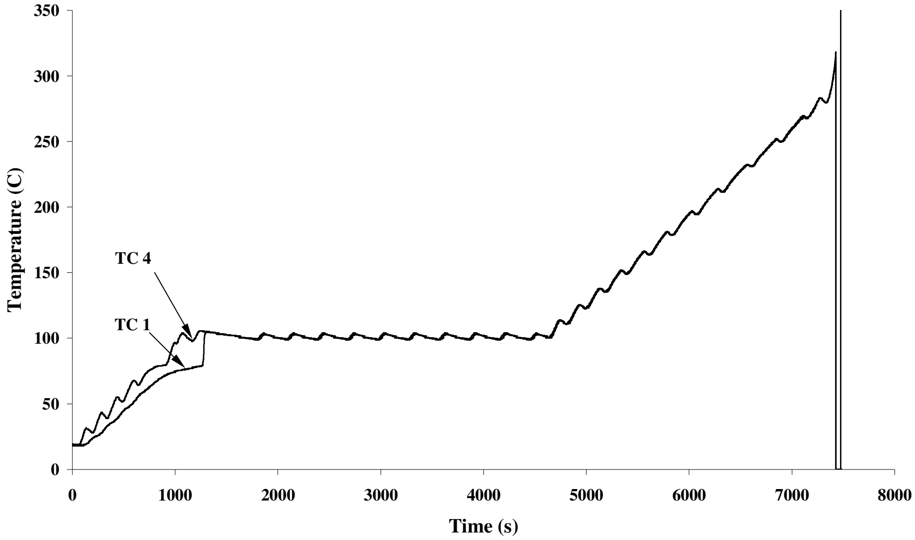

Figure AIII.2 - Small Scale Fast Cook-Off of a TNT Charge - 15% Void.

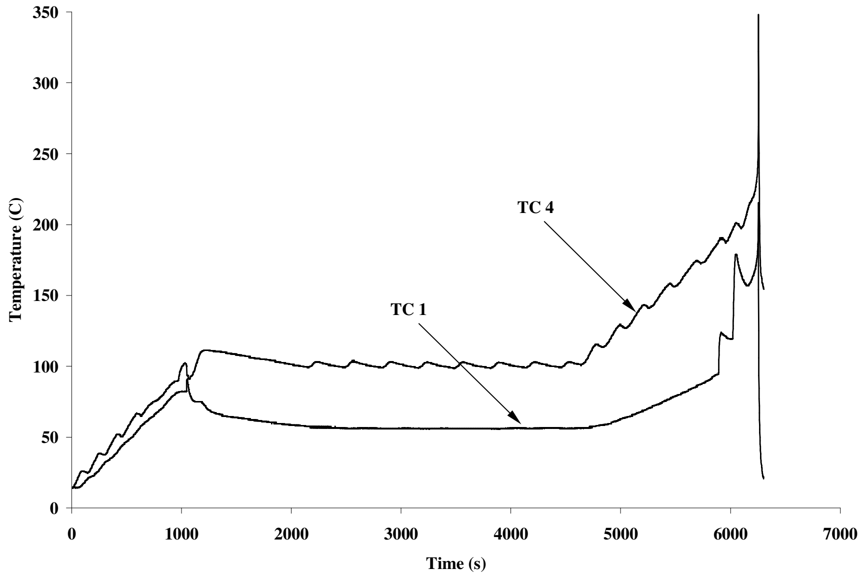

Figure AIII.3 - Small Scale Fast Cook-Off of a 25 RDX/75 TNT Charge - Invalid Test.

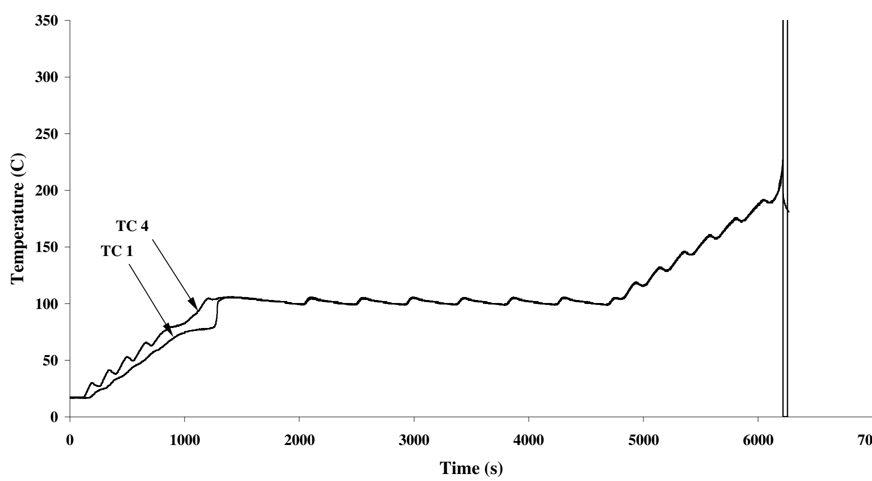

Figure AIII.4 - Small Scale Fast Cook-Off of a 25 RDX/75 TNT Charge.

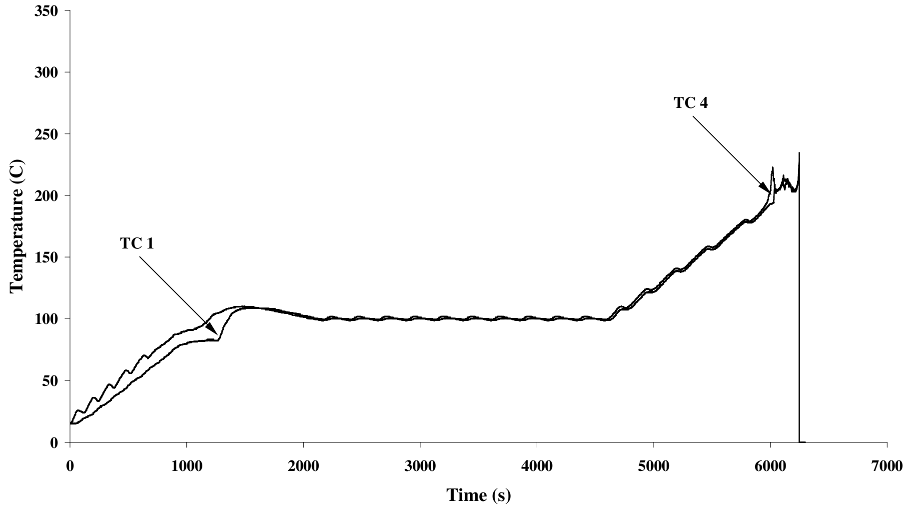

Figure AIII.5 - Small Scale Fast Cook-Off of a 40 RDX/60 TNT Charge.

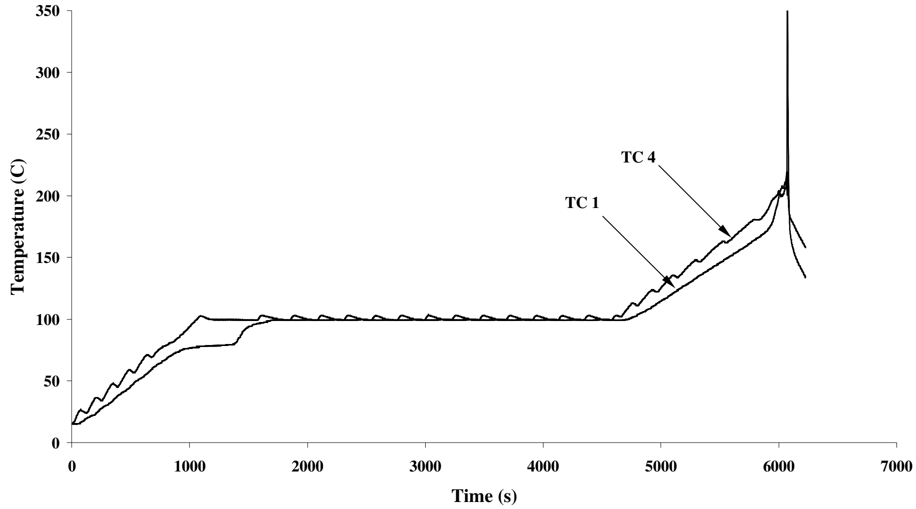

Figure AIII.6 - Small Scale Fast Cook-Off of a 50 RDX/50 TNT Charge.

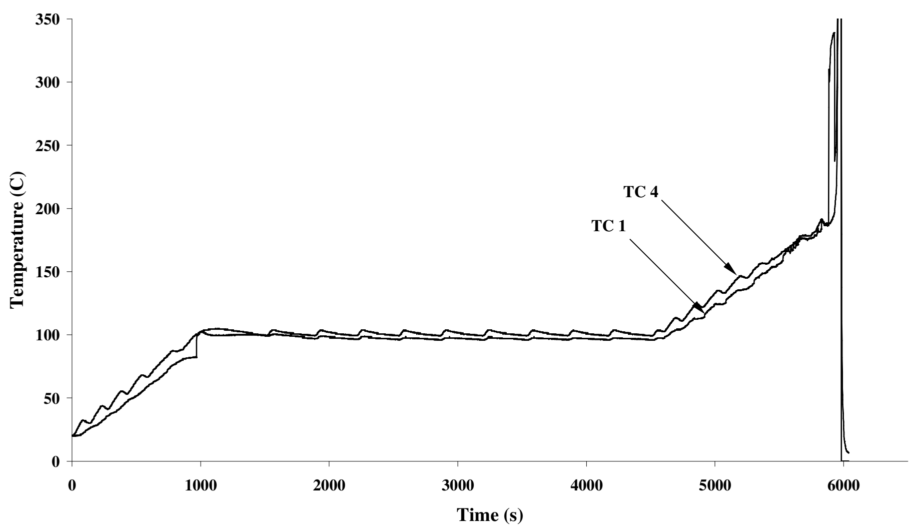

Figure AIII.7 - Small Scale Fast Cook-Off of a 60 RDX/40 TNT Charge.

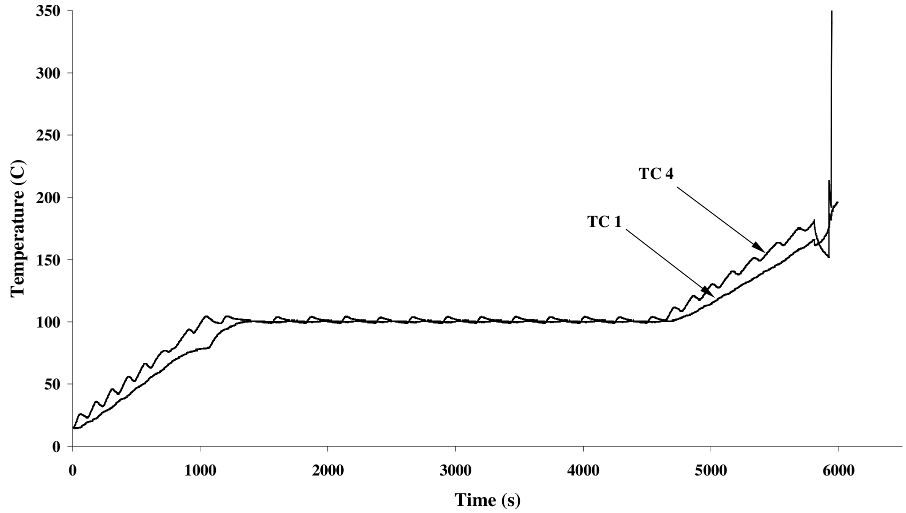

Figure AIII.8 - Small Scale Fast Cook-Off of a 75 RDX/25 TNT Charge.

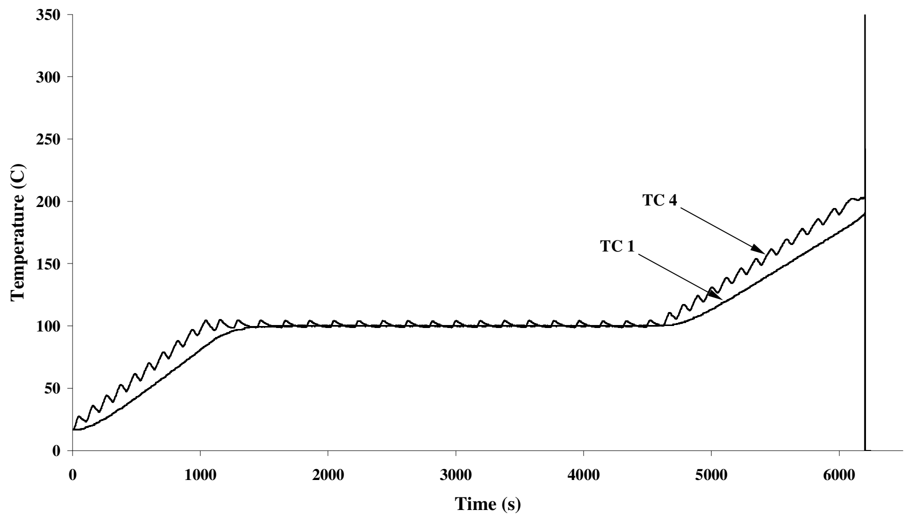

Figure AIII.9 - Small Scale Fast Cook-Off of a RDX Charge.

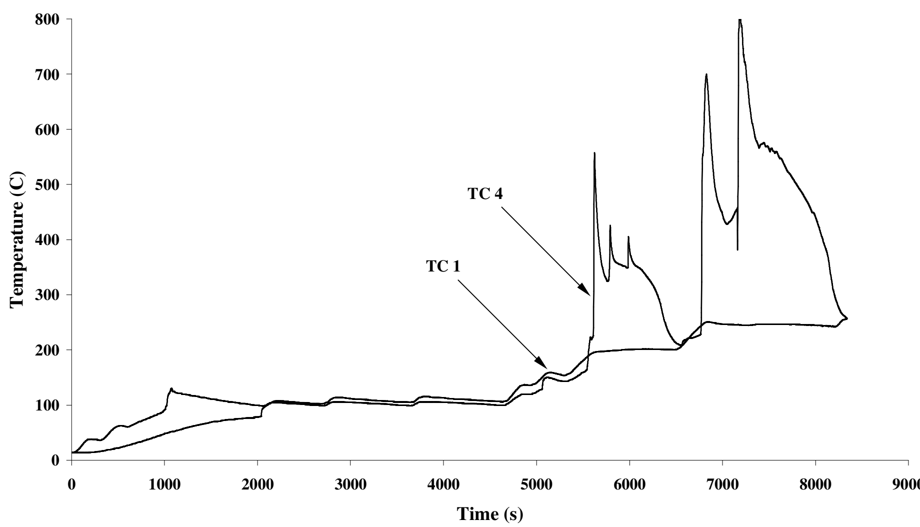

Figure AIII.10 - Medium Scale Fast Cook-Off of a TNT Charge.

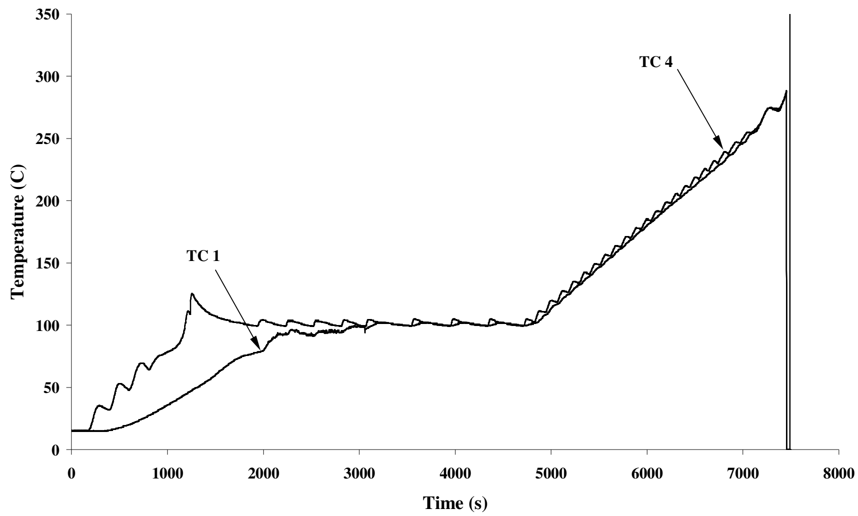

Figure AIII.11 - Medium Scale Fast Cook-Off of a TNT Charge - 15% Void.

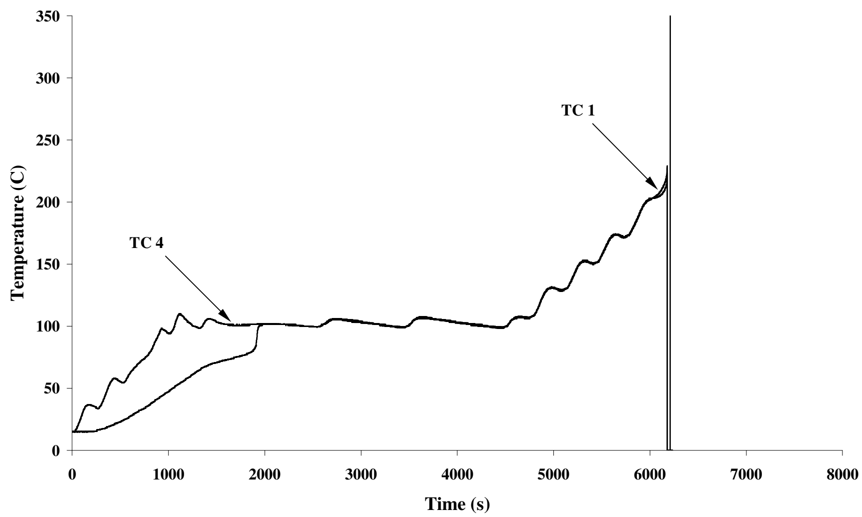

Figure AIII.12 - Medium Scale Fast Cook-Off of a 25 RDX/75 TNT Charge.

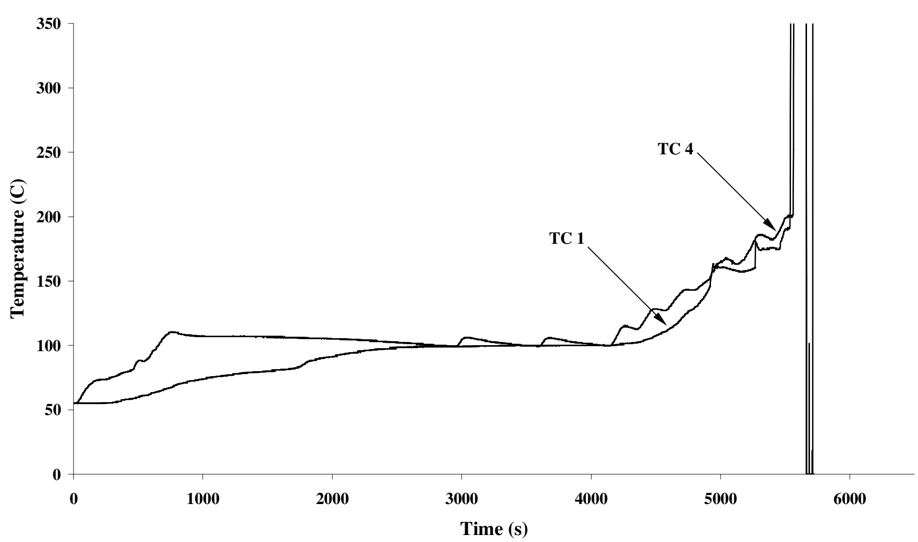

Figure AIII.13 - Medium Scale Fast Cook-Off of a 40 RDX/60 TNT Charge.

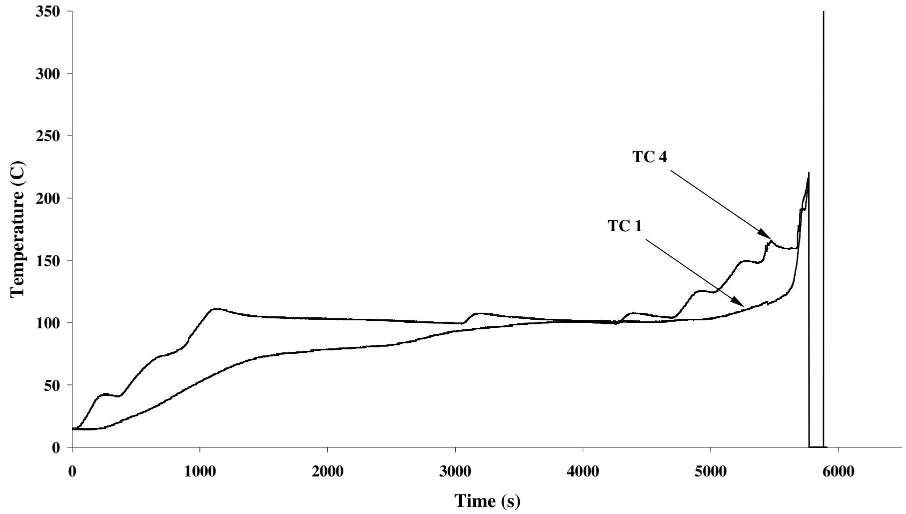

Figure AIII.14 - Medium Scale Fast Cook-Off of a 50 RDX/50 TNT Charge.

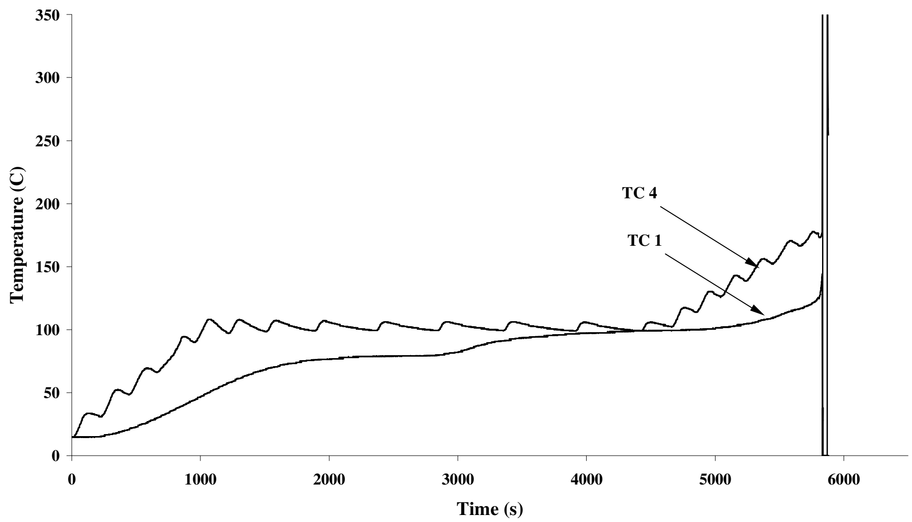

Figure AIII.15 - Medium Scale Fast Cook-Off of a 60 RDX/40 TNT Charge.

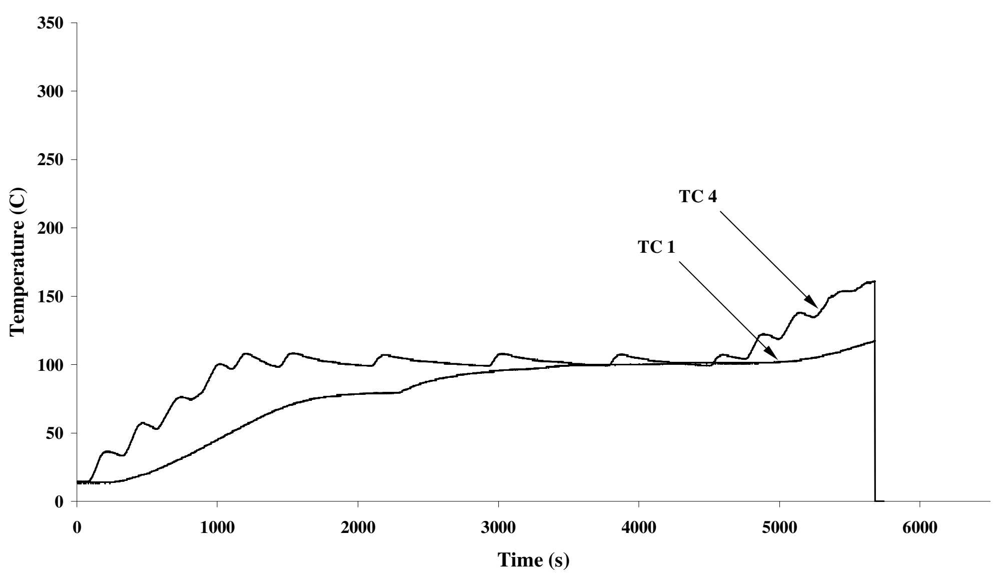

Figure AIII.16 - Medium Scale Fast Cook-Off of a 75 RDX/25 TNT Charge.

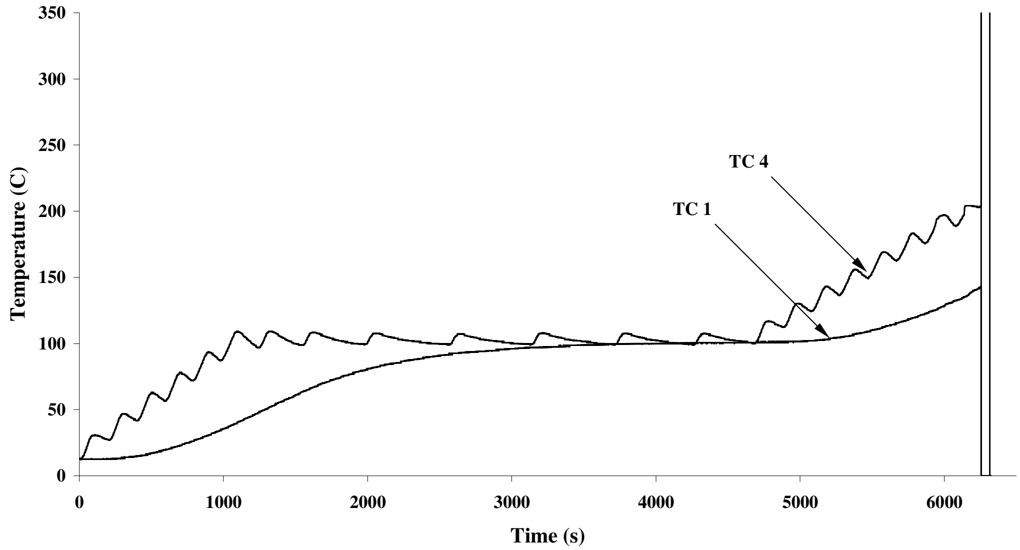

Figure AIII.17 - Medium Scale Fast Cook-Off of a RDX Charge.

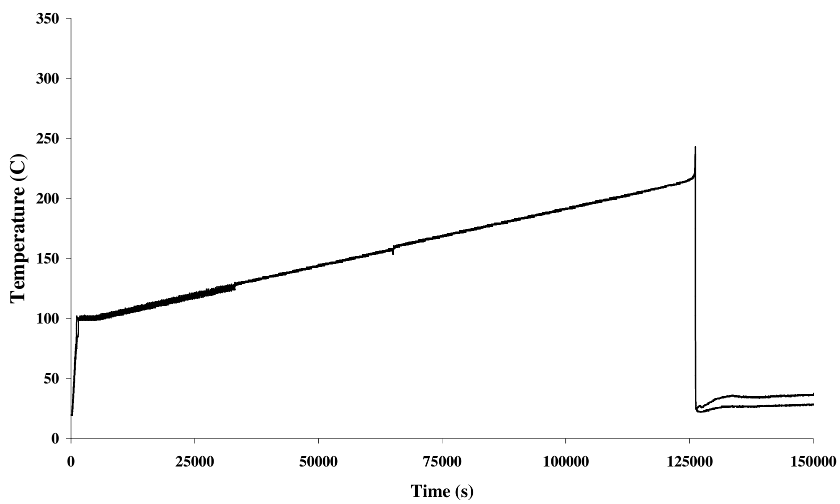

Figure AIII.18 - Small Scale Slow Cook-Off of a TNT Charge.

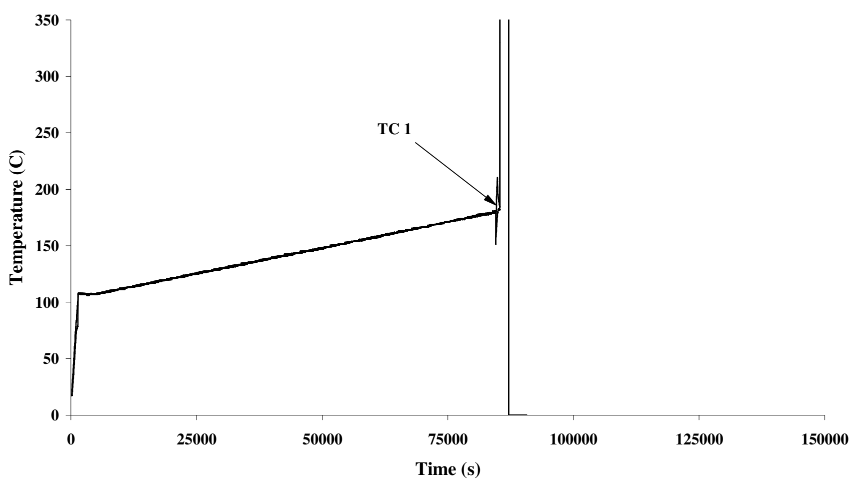

Figure AIII.19 - Small Scale Slow Cook-Off of a 25 RDX/75 TNT Charge.

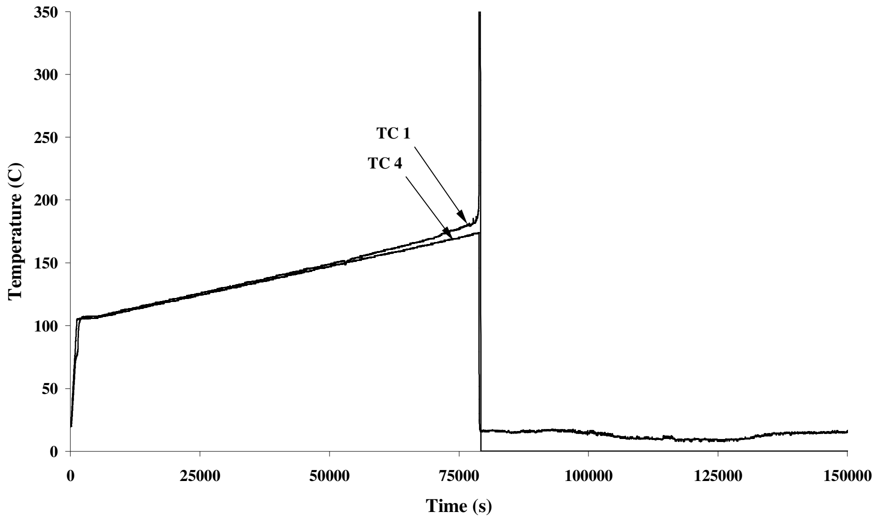

Figure AIII.20 - Small Scale Slow Cook-Off of a 40 RDX/60 TNT Charge.

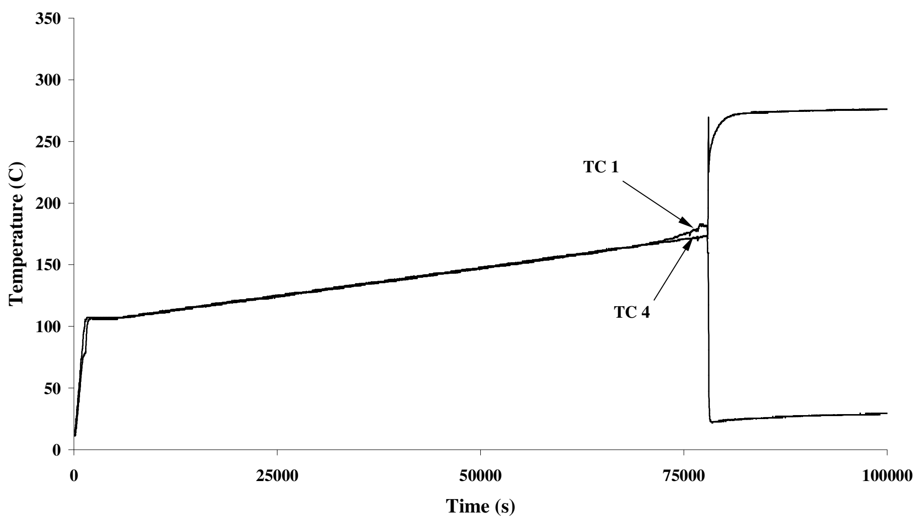

Figure AIII.21 - Small Scale Slow Cook-Off of a 50 RDX/50 TNT Charge.

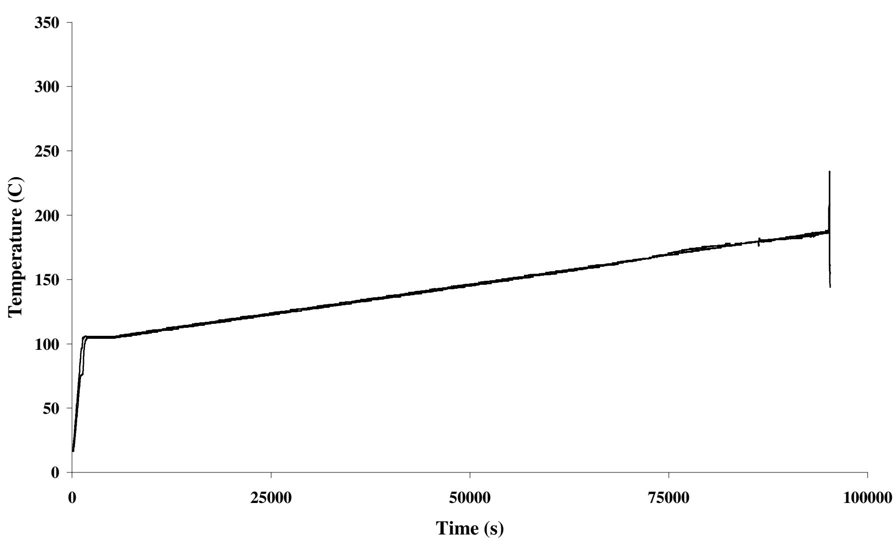

Figure AIII.22 - Small Scale Slow Cook-Off of a 60 RDX/40 TNT Charge.

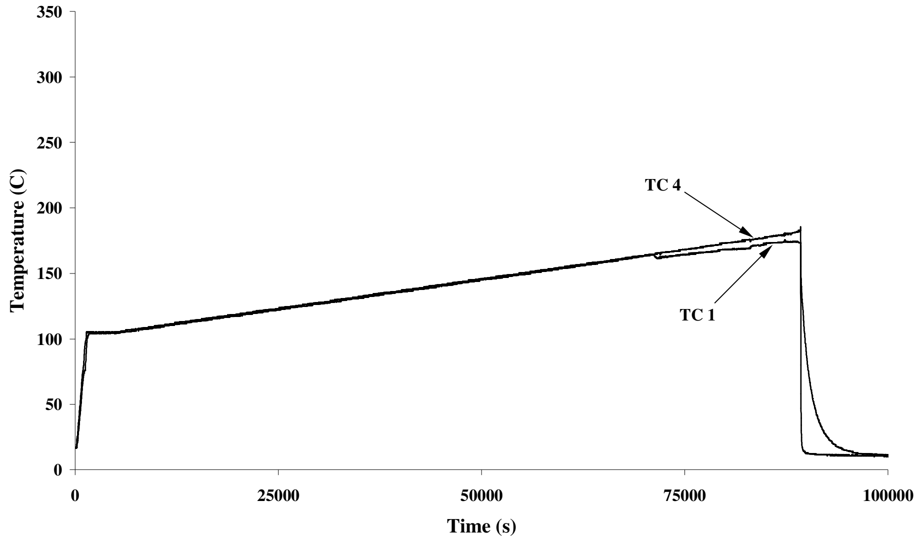

Figure AIII.23 - Small Scale Slow Cook-Off of a 75 RDX/25 TNT Charge.

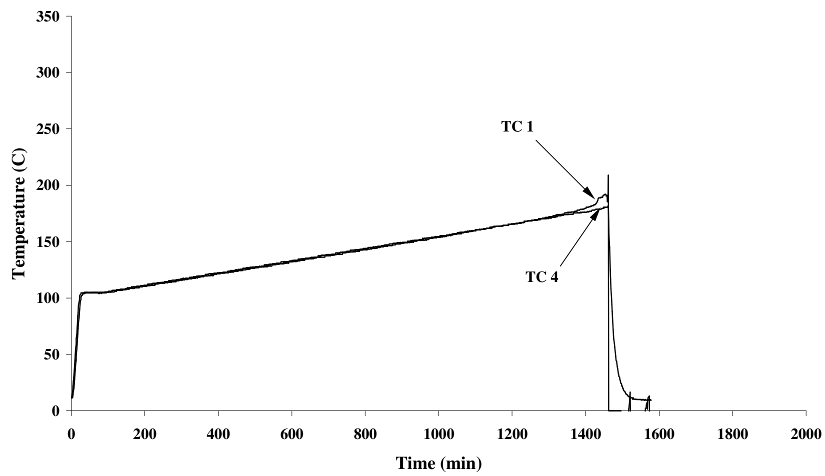

Figure AIII.24 - Small Scale Slow Cook-Off of a RDX Charge.

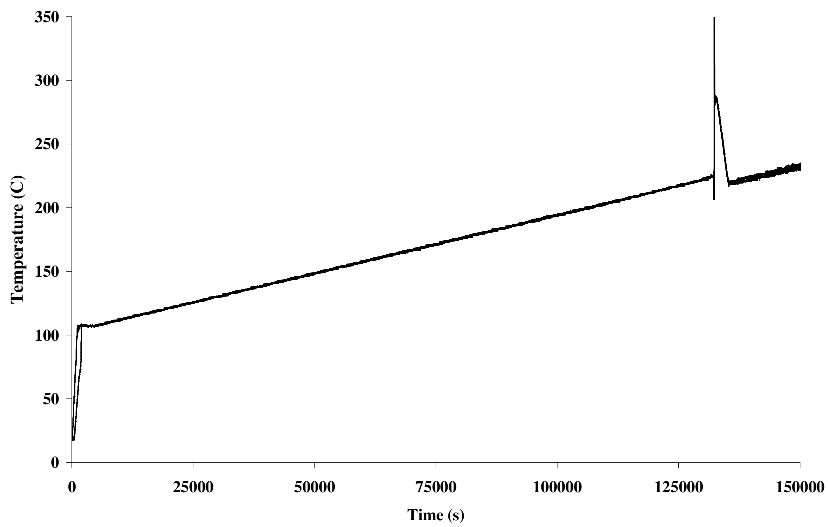

Figure AIII.25 - Medium Scale Slow Cook-Off of a TNT Charge.

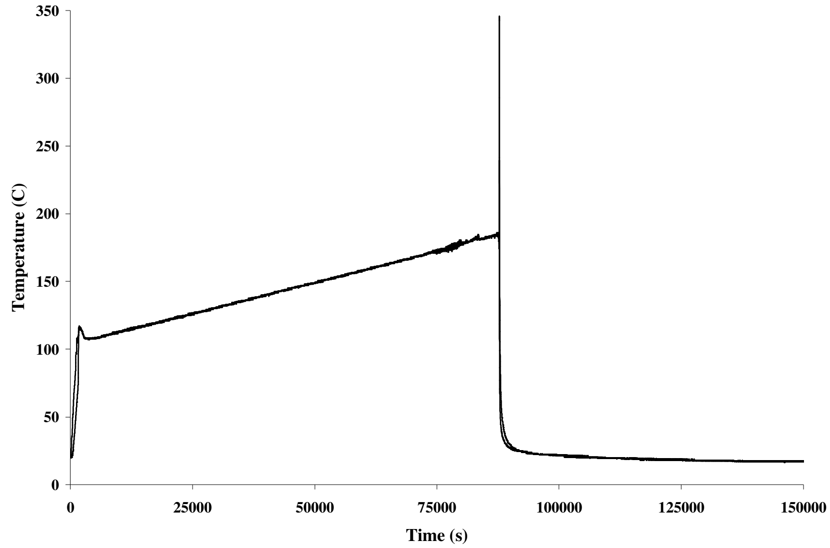

Figure AIII.26 - Medium Scale Slow Cook-Off of a 25 RDX/75 TNT Charge.

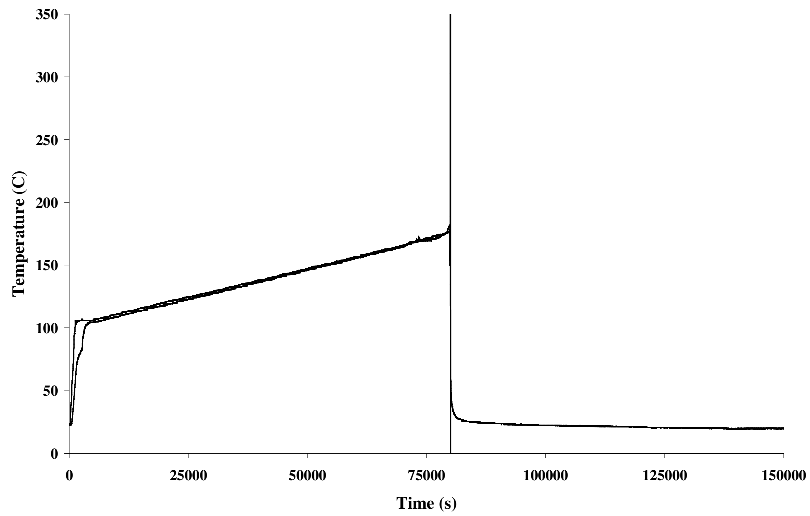

Figure AIII.27 - Medium Scale Slow Cook-Off of a 40 RDX/60 TNT Charge.

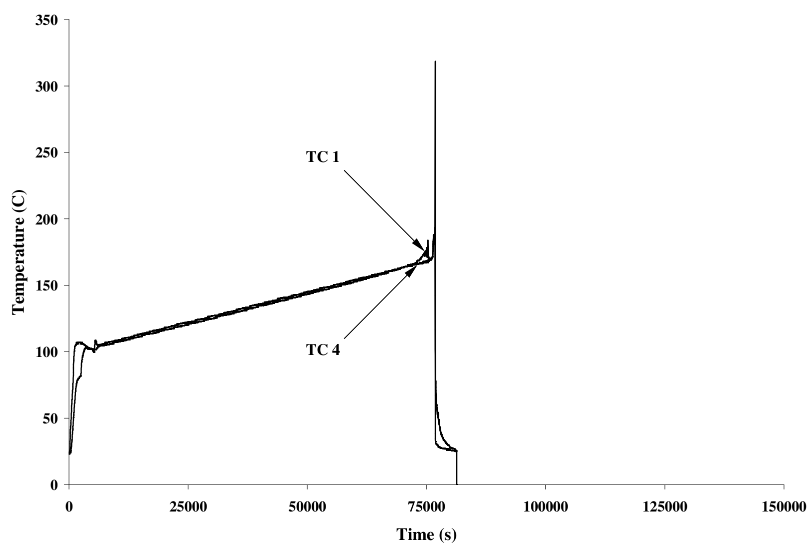

Figure AIII.28 - Medium Scale Slow Cook-Off of a 50 RDX/50 TNT Charge.

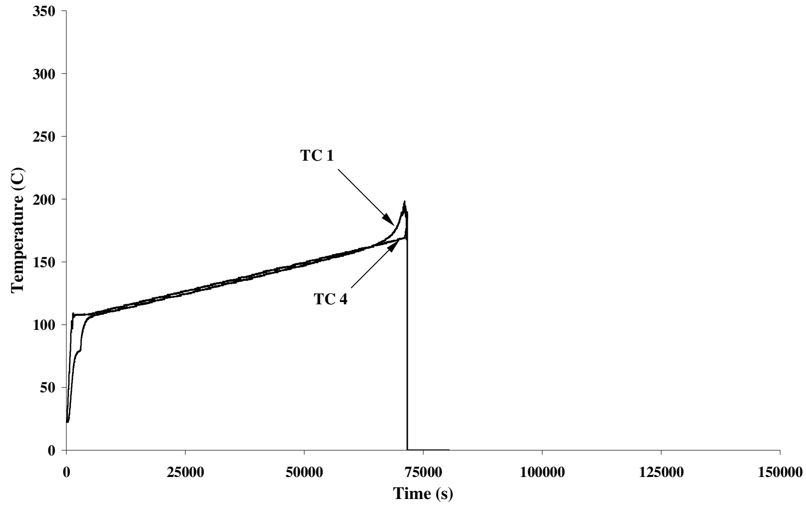

Figure AIII.29 - Medium Scale Slow Cook-Off of a 60 RDX/40 TNT Charge.

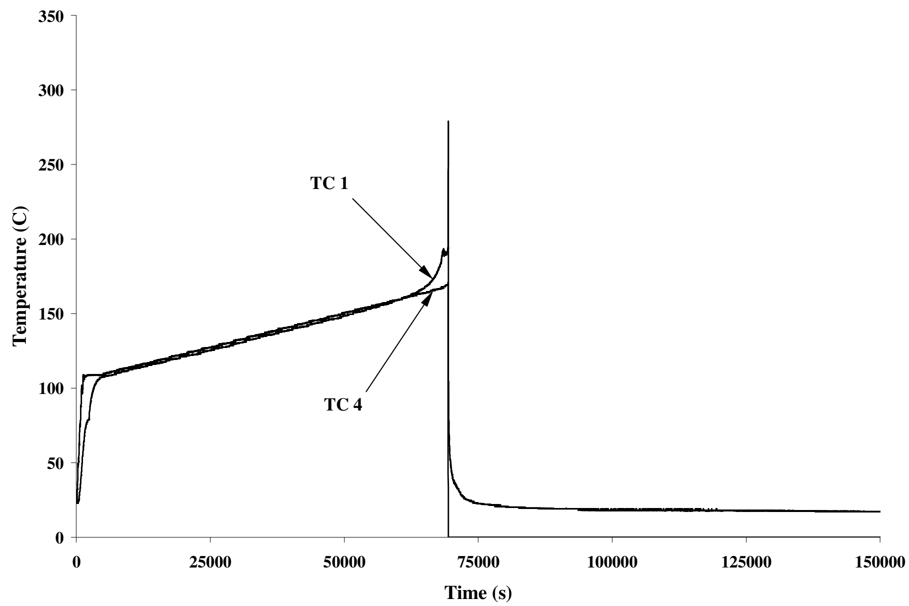

Figure AIII.30 - Medium Scale Slow Cook-Off of a 75 RDX/25 TNT Charge.

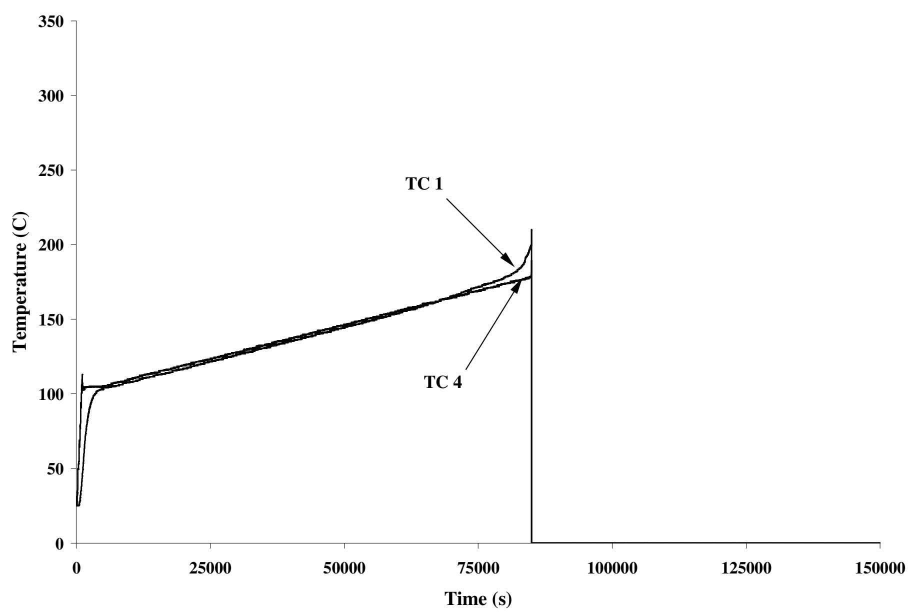

Figure AIII.31 - Medium Scale Slow Cook-Off of a RDX Charge.

Appendix IV

FRAGMENTATION ANALYSIS

The violence of event of the samples tested was qualitatively assessed on the basis of a visual examination of the types of fragments produced (see Chapter III - Section 3.6). The descriptors used are:

- Pressure Release - no fragments and only slight distortion of the vessel;
- Pressure Burst - no fragments, but disrupted and distorted vessel;
- Deflagration - large fragments;
- Detonation - small fragments.

For convenience, the following scheme of presentation was selected:

- Fast Cook-Off
    - Small Scale: Figures AIV.1 - AIV.8
    - Medium Scale: Figures AIV.9 - AIV.16
- Slow Cook-Off
    - Small Scale: Figures AIV.17 - AIV.23
    - Medium Scale: Figures AIV.24 - AIV.30

The recovered pieces were arranged by type on A4 sheets of paper and photographed as a group (Figs AIV.1 - AIV.30). The photographs show separately:

- recovered thermocouples, whenever they were not still attached to the top end cap;

- heating wire, with the possibility of having the test vehicle's body attached;

- remains of bolts, nuts and bolts' washers;

- top and bottom end caps (with or without thermocouples, with or without remains of the protective disk of the operational configuration, an in very exceptional cases with remains of the vehicle engine gasket washers);

- in those cases where fragmentation of the test vehicle's body occurred 5th and 6th sheets were used to spread the fragments divided by the following sieving ranges: $\geq$ 2500 µm, between 1405 - 2500 µm and <1405 µm. In very exceptional cases metallic dust is also include on an extra sheet;

- in some cases the remains of the protective disk of the operational configuration and remains of Rock Wool are presented on separate sheets.

In some photos a red arrow has been used to highlight the body of the test vehicle.

The results obtained for this study on the assessment of the violence of response are included in Tables AIV.1 and AIV.2:

	SMALL SCALE	MEDIUM SCALE
Sample	Type of Response	Type of Response
RDX	**Detonation**	**Detonation**
75RDX/25TNT	**Deflagration**	**Deflagration**
60RDX/40TNT	**Deflagration**	**Deflagration**
50RDX/50TNT	**Pressure Burst**	**Deflagration**
40RDX/60TNT	**Deflagration**	**Deflagration**
25RDX/75TNT	**Deflagration**	**Deflagration**
TNT	**Pressure Release**	**Pressure Release**
$TNT_{15\%void}$	**Pressure Burst**	**Deflagration**

Table AIV.1 - Qualitative Assessment on the Violence of Response of the Explosives Tested on the Fast Cook-Off Program.

These results show that, under fast cook-off at small scale, the violence of response of RDX/TNT mixtures tends to increase with increasing RDX content in the mixture, with the two exceptions being: 50 RDX/50 TNT and 75 RDX/25 TNT. An explanation has not yet been found for these two observed cases.

For the medium scale, the same trend is observable, although the 60 RDX/40 TNT mixtures appeared to behave somewhat less violently than its neighbours.

Concerning the effect of scale on the violence of response one can observe that, in most cases, there is an increase of the violence of response with the increase in the dimensions of the test vehicles.

For the slow cook-off program (see Table AIV.2), the results obtained indicate that, at small scale there is no significant difference in the violence of response for low to moderate RDX content (25 - 50%). At medium scale a similar situation occurs for the mixtures with RDX content varying between 25% and 60%.

Nevertheless, when the effect of scale has to be taken into consideration, there is a similar trend to the one observed for the fast cook-off program: there is, in most cases, an increase in violence of response with the increase in the dimensions of the vehicle.

	SMALL SCALE	MEDIUM SCALE
Sample	**Type of Response**	**Type of Response**
RDX	Deflagration	Detonation
75RDX/25TNT	Deflagration	Pressure Burst
60RDX/40TNT	Deflagration	Pressure Burst
50RDX/50TNT	Pressure Release	Pressure Burst
40RDX/60TNT	Pressure Release	Pressure Burst
25RDX/75TNT	Pressure Release	Pressure Burst
TNT	Pressure Release	Pressure Release

Table AIV.2 - Qualitative Assessment on the Violence of Response of the Explosives Tested on the Slow Cook-Off Program.

The type of response presented in Tables AIV.1 and AIV.2 should not be taken as definitive for these systems. Any study on violence of response necessarily demands a more reproducible degree of confinement than the one likely to be achieved in the present study. Therefore, these designations represent only one possible qualitative assessment of the violence of response based on "hands-on experience" type of assessment. For further studies of fragmentation analysis to be conducted in order to adequately assess and quantify the violence of response obtained for these systems, a fully confined test vehicle would need to be designed and constructed.

Fast Cook-Off

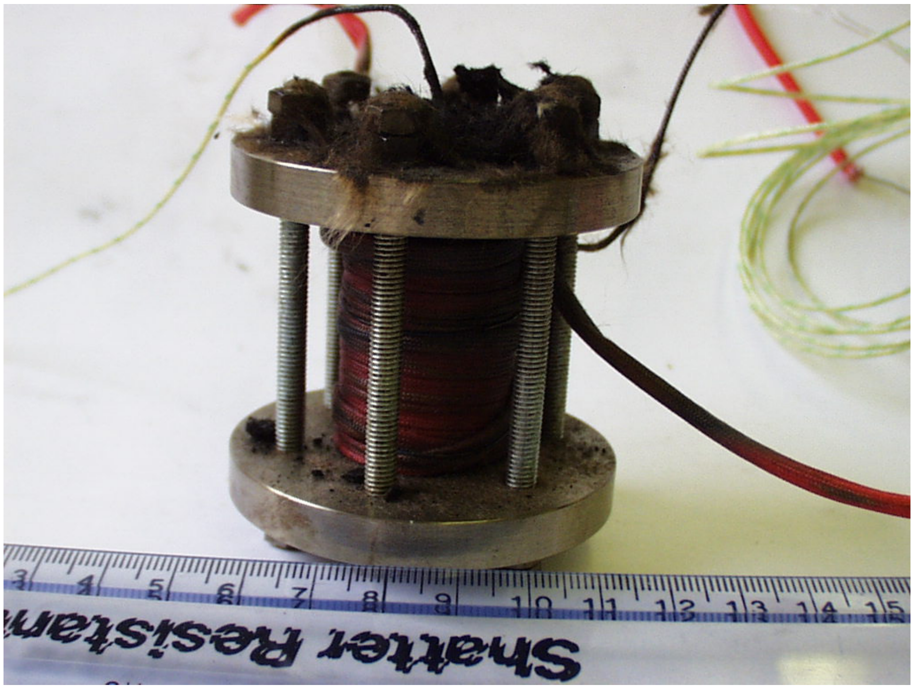

Figure AIV.1 - Small Scale Fast Cook-Off of a TNT Charge.

Figure AIV.2 - Small Scale Fast Cook-Off of a TNT Charge - 15% Void.

Figure AIV.3 - Small Scale Fast Cook-Off of a 25 RDX/75 TNT Charge.

Figure AIV.4 - Small Scale Fast Cook-Off of a 40 RDX/60 TNT Charge.

Figure AIV.5 - Small Scale Fast Cook-Off of a 50 RDX/50 TNT Charge.

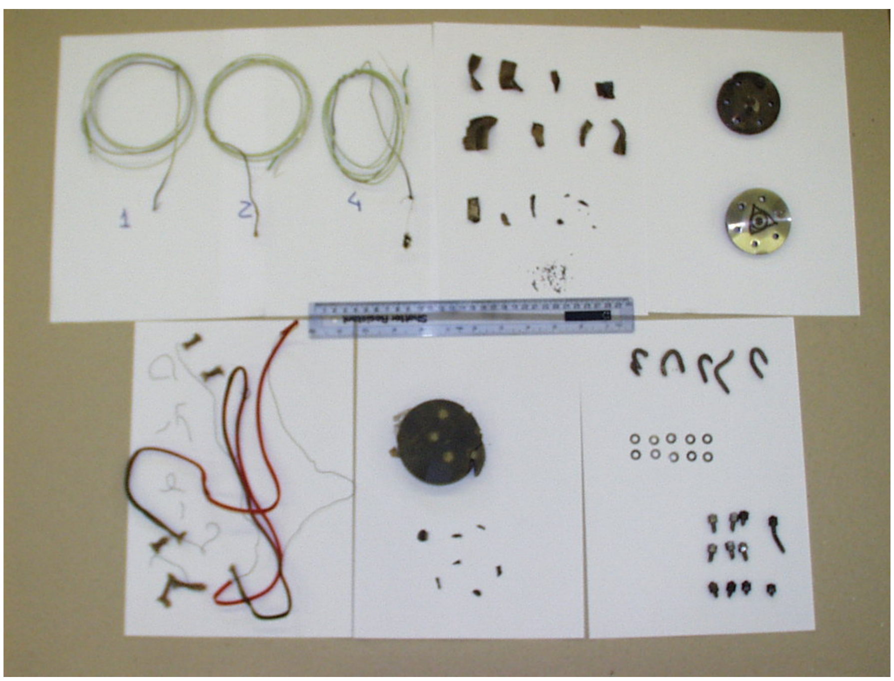

Figure AIV.6 - Small Scale Fast Cook-Off of a 60 RDX/40 TNT Charge.

Figure AIV.7 - Small Scale Fast Cook-Off of a 75 RDX/25 TNT Charge.

Figure AIV.8 - Small Scale Fast Cook-Off of a RDX Charge.

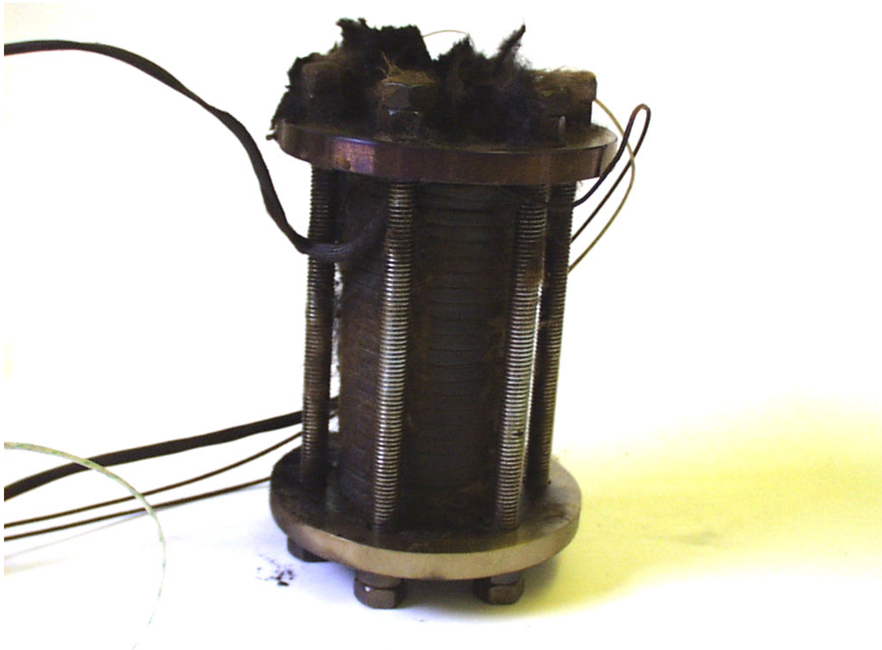

Figure AIV.9 - Medium Scale Fast Cook-Off of a TNT Charge.

Figure AIV.10 - Medium Scale Fast Cook-Off of a TNT Charge - 15% Void.

Figure AIV.11 - Medium Scale Fast Cook-Off of a 25 RDX/75 TNT Charge.

Figure AIV.12 - Medium Scale Fast Cook-Off of a 40 RDX/60 TNT Charge.

Figure AIV.13 - Medium Scale Fast Cook-Off of a 50 RDX/50 TNT Charge.

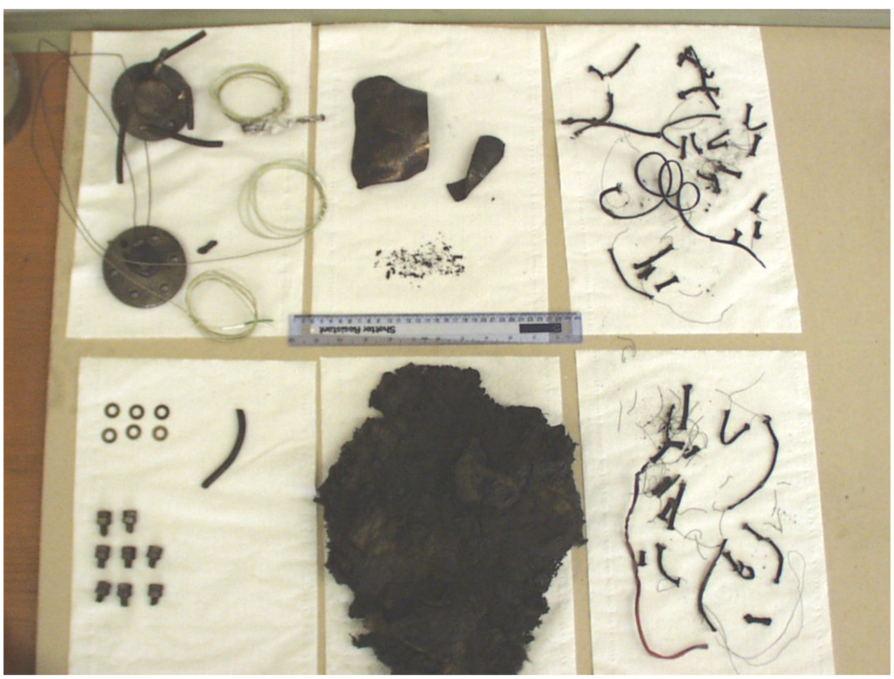

Figure AIV.14 - Medium Scale Fast Cook-Off of a 60 RDX/40 TNT Charge.

Figure AIV.15 - Medium Scale Fast Cook-Off of a 75 RDX/25 TNT Charge.

Figure AIV.16 - Medium Scale Fast Cook-Off of a RDX Charge.

Slow Cook-Off

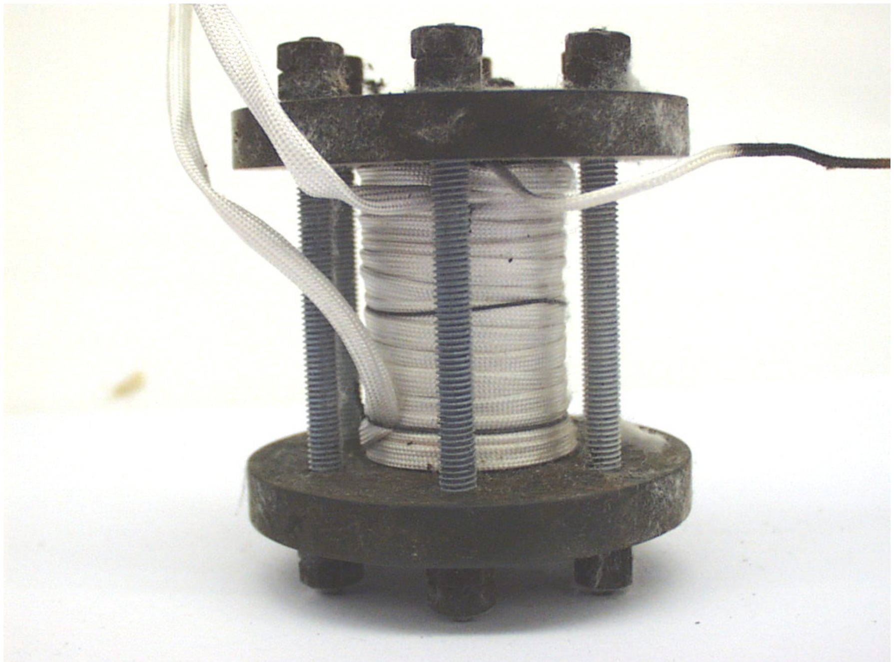

Figure AIV.17 - Small Scale Slow Cook-Off of a TNT Charge.

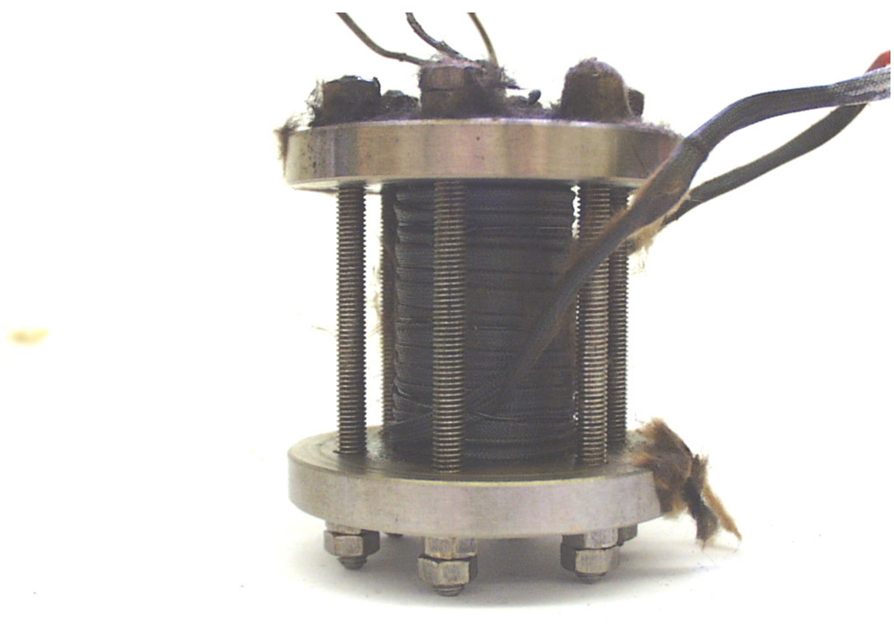

Figure AIV.18 - Small Scale Slow Cook-Off of a 25 RDX/75 TNT Charge.

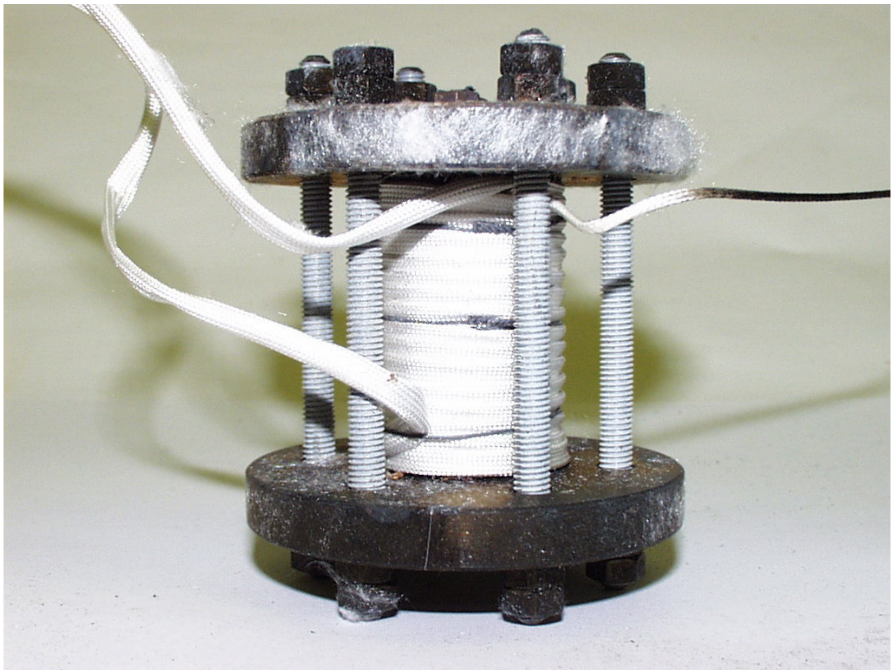

Figure AIV.19 - Small Scale Slow Cook-Off of a 40 RDX/60 TNT Charge.

Figure AIV.20 - Small Scale Slow Cook-Off of a 50 RDX/50 TNT Charge.

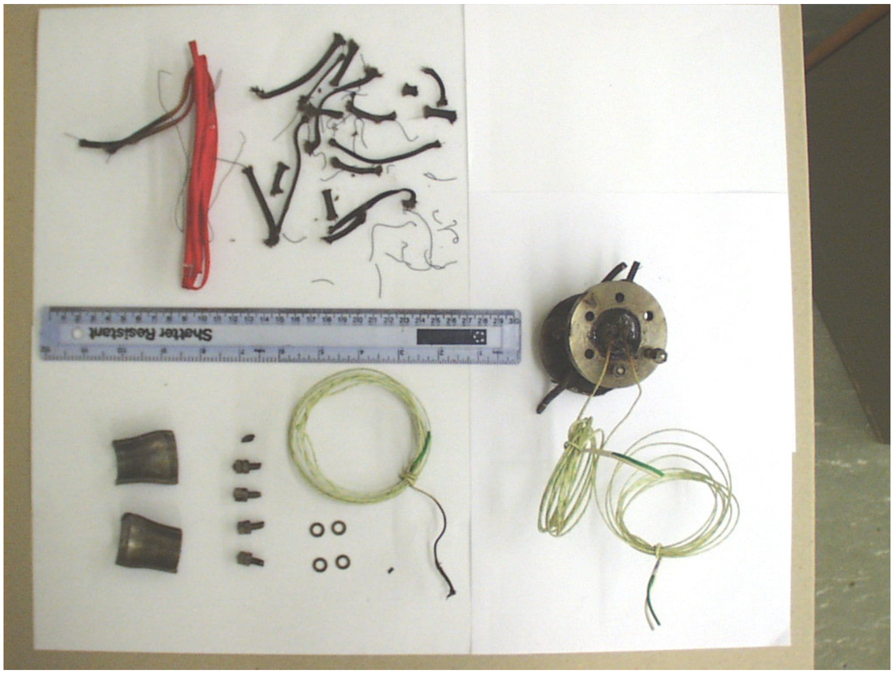

Figure AIV.21 - Small Scale Slow Cook-Off of a 60 RDX/40 TNT Charge.

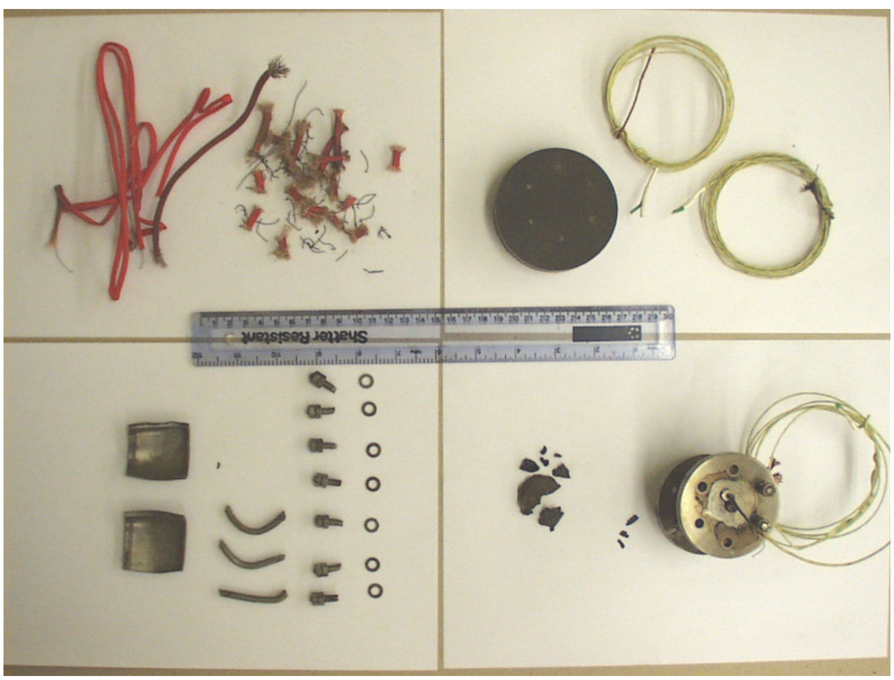

Figure AIV.22 - Small Scale Slow Cook-Off of a 75 RDX/25 TNT Charge.

Figure AIV.23 - Small Scale Slow Cook-Off of a RDX Charge.

Figure AIV.24 - Medium Scale Slow Cook-Off of a TNT Charge.

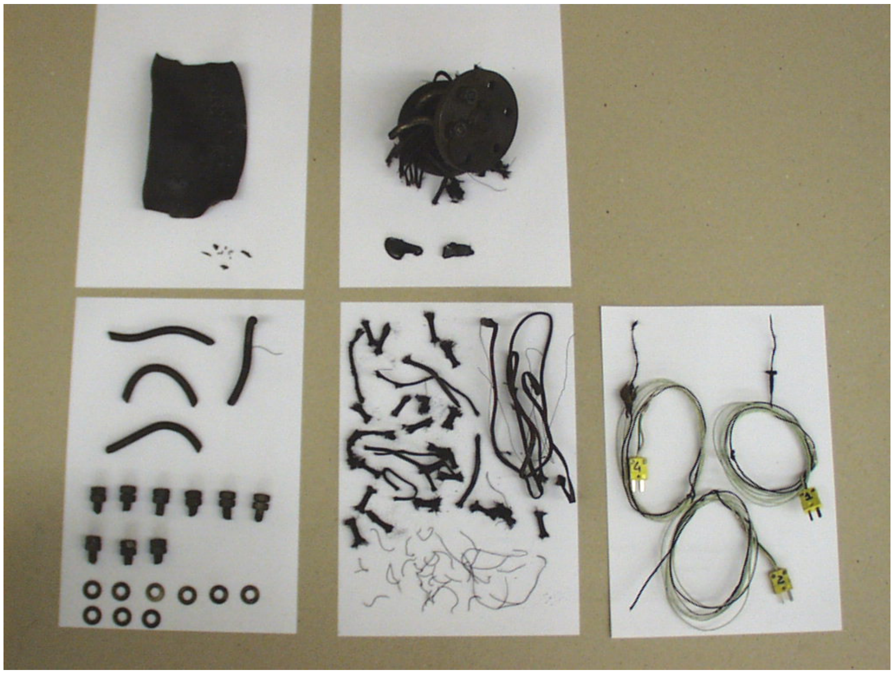

Figure AIV.25 - Medium Scale Slow Cook-Off of a 25 RDX/75 TNT Charge.

Figure AIV.26 - Medium Scale Slow Cook-Off of a 40 RDX/60 TNT Charge.

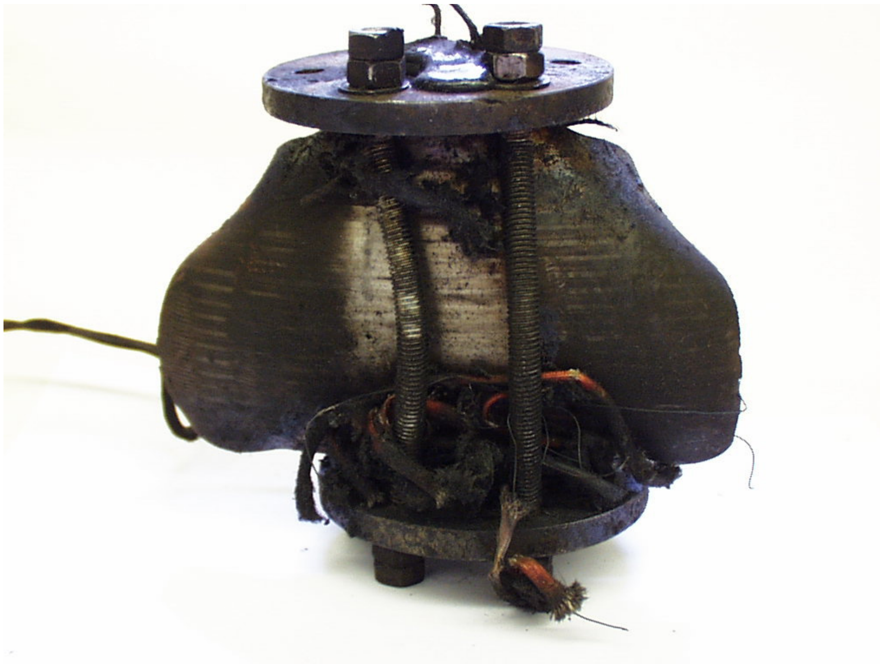

Figure AIV.27 - Medium Scale Slow Cook-Off of a 50 RDX/50 TNT Charge.

Figure AIV.28 - Medium Scale Slow Cook-Off of a 60 RDX/40 TNT Charge.

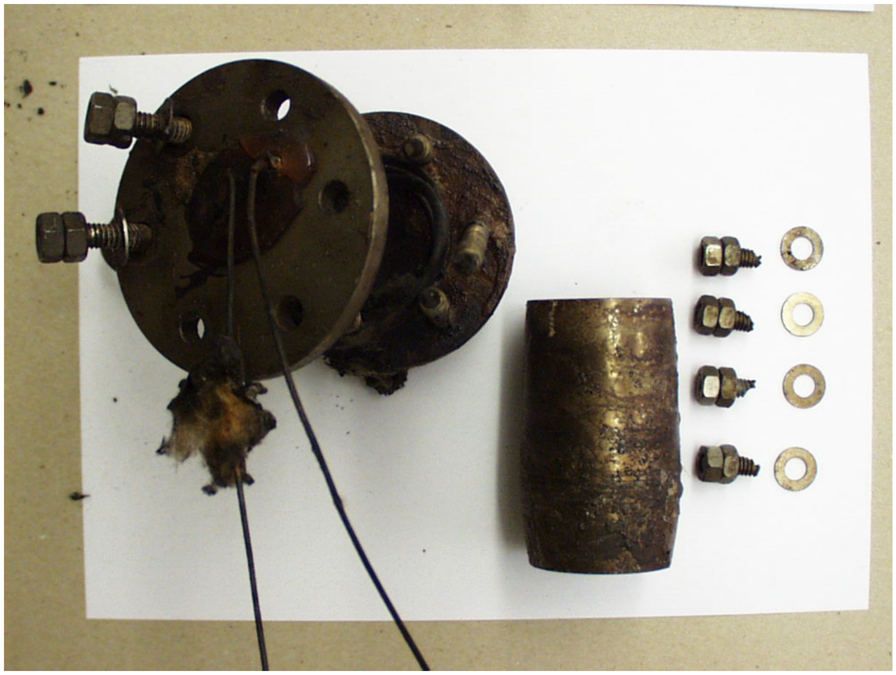

Figure AIV.29 - Medium Scale Slow Cook-Off of a 75 RDX/25 TNT Charge.

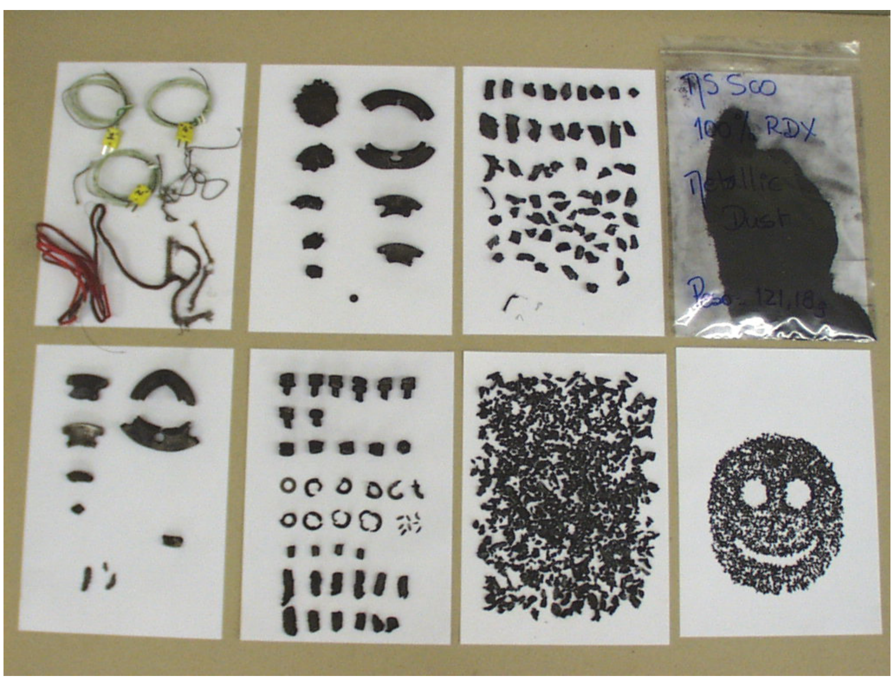

Figure AIV.30 - Medium Scale Slow Cook-Off of a RDX Charge.

Appendix V

PUBLICATIONS

The references of the publications presented in International Symposia and Seminars are enclosed in this Appendix.

The order of publication is the following:

- "**Thermal Cook-Off Studies on Explosives**" - with Bailey, A. & Cartwright, M.. In: *26th International Pyrotechnics Seminar***,** Proceedings, pp. 29 - 36, Nanjing, China, 1 - 4 October 1999.

- "**Small Scale Cook-Off Studies of Explosives**" - with Bailey, A.. In: *12th International Symposium on Chemical Problems Connected with the Stability of Explosives*, to be published in Proceedings, Karlsborg, Sweden, 13 - 17 May 2001.

- "**Effect of Scale on Cook-Off Studies of Explosives**" - with Bailey, A.. In: *28th International Pyrotechnics Seminar***,** Proceedings, pp. 321 - 331, Adelaide, Australia, 4 - 9 November 2001.

- "**Effect of Scale on Slow Cook-Off Studies of Explosives**" - with Davies, N. & Bailey, A.. In: To be published in the *29th International Pyrotechnics Seminar***,** Proceedings, to be held in Westminster, Colorado, USA, 14-19 July 2002.

[Awarded the Frank Carver Bursary as an Outstanding Young Scientist for this scientific paper.]

- "**The Use of a Low Cost Scalable Vehicle for Fast and Slow Cook-Off**" - with Davies, N. & Bailey, A.. In: To be published in the *29th International Pyrotechnics Seminar***,** Proceedings, to be held in Westminster, Colorado, USA, 14 - 19 July 2002.